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H. R. Cho and J. V. Iribarne

THE ROLE OF CLOUDS AND PRECIPITATION
IN LONG RANGE TRANSPORT AND ACID RAIN
IN EASTERN CANADA

II - CHEMISTRY

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THE ROLE OF CLOUDS AND PRECIPITATION
IN LONG RANGE TRANSPORT AND ACID RAIN
IN EASTERN CANADA

BY

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JUNE, 1983

ONTARIO HYDRO CONTRACT: P.O. NO. 12-30707-11

THE ROLE OF CLOUDS AND PRECIPITATION
IN LONG RANGE TRANSPORT AND ACID RAIN
IN EASTERN CANADA

PART II - CHEMISTRY

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THERMODYNAMIC AND CHEMICAL VARIABLES

In the next chapters, devoted to the analysis of equilibrium conditions and to chemical reactions and their rates, a number of variables will be used. They will be defined here, and some useful relations will be derived.

Thermodynamic variables

The following symbols will be used:

T = temperature, expressed either in Kelvin (K) or in degrees Celsius ($^{\circ}\text{C}$).

p = pressure

p_i = partial pressure of gaseous species i .

ρ = air density

ρ_w = water density = $1 \text{ g cm}^{-3} = 1 \text{ kg l}^{-1}$

e = water vapour pressure

l_v = latent heat of vaporization

c_p = specific heat capacity at constant pressure

m = mass

n = number of moles

μ_i = molecular weight of species i

μ_a = molecular weight of dry air = $28.964 \text{ g mol}^{-1}$

R_a = specific gas constant of dry air = $287.05 \text{ J kg}^{-1} \text{ K}^{-1}$

R = gas constant = $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$\epsilon = \mu_w / \mu_a = 0.622$, where μ_w = molecular weight of water = 18.02 g mol^{-1}

Subscripts

i = pertaining to chemical species i

a = pertaining to dry air

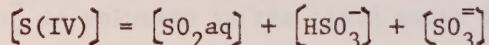
w = pertaining to water; also: water vapour saturation value

Concentrations and densities

For convenience, concentrations of water vapour, liquid water or ice and concentrations of various chemical species, when referred to the air, will be expressed mainly as mass mixing ratios C_i or as volume mixing ratios $C_i(v)$ (if they are gaseous).

When chemical species in solution are considered, concentrations are expressed as molarities, or eventually as normalities, and written $[i]$ for chemical species i (e.g. $[\text{HSO}_3^-]$ = moles of HSO_3^- per liter). $[i]$ is therefore always given in mol l^{-1} (or equiv.-g l^{-1}).

When the total amount dissolved may be given by the sum of various species, it will frequently be expressed indicating the valency, as in the following examples:



The same symbol with a subscript g (for gaseous phase) is used to indicate concentration of i in moles per unit volume of air: $[i]_g$.

Thus the list of concentration variables is:

r = water vapour mass mixing ratio

r_L = liquid water mass mixing ratio

r_S = ice mass mixing ratio

C_i = mass mixing ratio of chemical species i

$[i]$ = molar (or normal, if so indicated) concentration of species i in cloud water

$[i]_g$ = concentration of species i in air, in moles per unit volume

Molecular weights μ_i are given always in g mol^{-1} . Also, for convenience, the density of water is given as $\text{g cm}^{-3} = \text{kg l}^{-1}$ (rather than in kg m^{-3}); as its numerical value in these units is unity; it is only present in some formulas for reasons of dimensional homogeneity. The density of air is given by kg m^{-3} . This mixture of units lacks consistency, but was adopted for convenience. A factor 10^3 , frequently present, is a conversion factor in g kg^{-1} .

The following relations between the different types of concentrations will be frequently used:

$$C_i(V) = \frac{n_i}{n_a} = \frac{m_i/\mu_i}{m_a/\mu_a} = \frac{\mu_a}{\mu_i} C_i \quad (1)$$

$$p_i = C_i(V) p \quad (2)$$

If a concentration $[i]$ in solution in the cloud water is to be expressed as the mass of i per unit mass of air, i.e., as the equivalent mass mixing ratio, the relation is:

$$C_i = 10^{-3} \rho_w^{-1} \mu_i r_L [i] \quad (3)$$

where 10^{-3} converts g to kg , ρ_w is the solution density in g cm^{-3} , and μ_i is given in g mol^{-1} . If the volume mixing ratio is used:

$$C_i(V) = 10^{-3} \rho_w^{-1} \mu_a r_L [i] \quad (4)$$

The relation of equivalence between $[i]$ and the volume mixing ratio $C_i(V)$ indicating, for instance, what concentration $[i]$ in the liquid phase will produce total dissolution of species i initially present in the air at concentration $C_i(V)$, is given by:

$$[i] = \frac{10^3 \rho_w c_i(V)}{\mu_a r_L} = 34.56 \frac{c_i(V)}{r_L} \quad (5)$$

The relations between $[i]_g$ and mixing ratios in the air are given by

$$[i]_g = \frac{n_i}{V} = \frac{p}{RT} c_i(V) \quad (6)$$

$$= \frac{\mu_a}{\mu_i} \frac{p}{RT} c_i \quad (7)$$

I. EQUILIBRIUM CONDITIONS

1. Cloud parameters
2. Constants used
3. Influence of aerosol alkalinity
4. SO_2 dissolving in pure water
5. System with SO_2 , NH_3 and aerosol alkalinity
6. System with SO_2 and NH_3 in amounts limited to an initial input, and aerosol alkalinity
7. Equilibrium of CO_2
8. System with SO_2 and NH_3 in amounts limited to an initial input, CO_2 and aerosol alkalinity
9. Examples of solution for the system with SO_2 and NH_3 in amounts limited to an initial input, without and with CO_2 .
No aerosol alkalinity ($\text{Alk}=0$).
10. Simplified treatment of equilibrium
11. The effect of acidity on the distribution of SO_2 between the two phases
12. Conclusions

EQUILIBRIUM BETWEEN LIQUID AND GASEOUS PHASES

AND IN THE LIQUID

Although the processes occurring in a cloud, including dissolution of chemical species into the cloud water and chemical reactions in liquid phase, are essentially dynamic, a study of certain equilibria provide a background that must be kept in mind. Besides, the establishment of equilibria between the two phases is usually fast enough compared with the air motions and the chemical reactions taking place, so that essentially a state of equilibrium may be assumed within the cloud, as will be shown in Ch. III.

For these reasons, this study will start by an analysis of the equilibria involving SO_2 , which are of foremost importance. They are also relatively complex, as they involve not only the equilibrium of a certain species between the two phases, but also the various ionic equilibria in solution. Other equilibria, involving only molecular species (or involving only negligible ionizations in solution) such as those of the solubility of H_2O_2 and O_3 , are much simpler. The equilibria involving nitrogen compounds are quite complicated, partly not well known, and for reasons to be explained later (low solubility of nitrogen oxides, slow reactions: see chapter on in-cloud chemistry) they do not seem to warrant a preliminary examination at this stage.

Therefore, this chapter will deal with the solubility and ionic equilibria of SO_2 , alone or in the presence of NH_3 and CO_2 . No oxidation reactions are considered, and no oxidants are assumed present, apart from the air oxygen.

1. Cloud parameters

In order to perform a limited number of computations, so as to be able to derive a picture of the influence of various chemical parameters, a model of atmosphere has been assumed: the ICAO Standard Atmosphere (see for instance Iribarne and Godson, 1981, p.166). It can be described by the first three columns of Table 1. The last column indicates the water vapour saturation mixing ratio r_w corresponding to each temperature and pressure. We assume that humid air is injected from below in this atmosphere forming a cloud with the base at 800 mb and the top perhaps at 400 or 300 mb (5 to 7 km higher). We further assume for simplicity that the ascent is adiabatic. That indicates that $r_L = 4.3$ g/kg are to be expected at 500 mb and 5 to 5.5 g/kg at the top. In the examples to be worked out the choice has been made of $p = 0.6$ atm and $r_L = 5 \times 10^{-3} = 5$ g/kg.

Table 1

p(mb)	Z(m)	T(°C)	r_w (g/kg)
300	9160	-44.5	0.24
400	7180	-31.7	0.67
500	5570	-21.2	1.4
600	4200	-12.3	2.5
700	3010	- 4.6	3.9
800	1950	2.3	5.7
900	990	8.6	7.8
1013.25	0	15.0	10.6

If air is ascending at an average vertical velocity of 2 m/s through an area of $R = 3$ km radius, the air influx is 5.6×10^7 kg/s. The cloud

has a total mass equal to $\pi R^2(p_b - p_t)/g$ (where p_b is the base pressure, p_t the top pressure and g is the gravity acceleration), which gives $\sim 1.3 \times 10^{11}$ kg. Then the average permanency of an air parcel in the cloud is $1.3 \times 10^{11}/5.6 \times 10^7 = 2320 \text{ s} \approx 39 \text{ min}$. As water condenses gradually along the ascent, the average permanency of every mass element of liquid water can be estimated around 20 min. These relations will be better analyzed in the chapter on mass budgets, and these figures are only mentioned here to determine the order of magnitude of some parameters. It is assumed in particular that the equilibria about to be analyzed may be established in times $\ll 20 \text{ min}$.

2. Constants used

In the following examples, the following set of constants has been used, corresponding to a temperature of 0°C .

$$K_1 = \frac{[\text{HSO}_3^-][\text{H}^+]}{[\text{H}_2\text{SO}_3]} = 3.1 \times 10^{-2} \text{ M}$$

$$K_2 = \frac{[\text{SO}_3^{=2-}][\text{H}^+]}{[\text{HSO}_3^-]} \approx 2.05 \times 10^{-7} \text{ M (estimated by extrapolation)}$$

$$K_{\text{NH}_3} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = 1.374 \times 10^{-5} \text{ M}$$

$$K_w = [\text{H}^+][\text{OH}^-] = 1.14 \times 10^{-15} \text{ M}^2$$

$$H = \frac{[\text{H}_2\text{SO}_3]}{p_{\text{SO}_2}} = 3.28 \text{ M atm}^{-1}$$

$$H_{\text{NH}_3} = \frac{[\text{NH}_4\text{OH}]}{p_{\text{NH}_3}} = 23 \text{ M atm}^{-1}$$

Several remarks must be made on this set. All concentrations are in molarity, and the equilibrium constants have the corresponding units. K_2 is a rough approximation, but the second ionization plays only a very secondary role in the range of pH of interest, so that an error in the constant is not important. Of more consequence is that the value taken for H_{NH_3} is possibly near ten times smaller than later, and presumably better, measurements. However, as it turns out for the estimates of equilibrium attained with a limited initial supply of gaseous NH_3 (the case of interest in a cloud), most of the available NH_3 becomes dissolved in the liquid phase in all but 2 example computations (#8 and 9) when still more than half is dissolved. Thus correcting this constant with the newer value will change very little the picture obtained and practically nothing of the conclusions for the case of limited amount of SO_2 and NH_3 in the gas phase.

The concentration of dissolved undissociated SO_2 has been written $[H_2SO_3]$, although this is probably not the actual molecular species formed in solution.⁽¹⁾ Some authors prefer for that reason to write $[SO_2(aq)]$ or some similar expression. Without presupposing anything about the structure of the compound, both expressions are taken here as referring identically to the same species.

3. Influence of aerosol alkalinity

As it is well known, cloud droplets form by condensation on a small fraction of the atmospheric aerosol particles that become activated at the water vapour supersaturations reached by the ascending air. The saturation vapour pressure of droplets formed on dissolving hygroscopic nuclei depend both

(1) In this, the common use in chemistry is followed, where H_2SO_3 as a symbol does not necessarily imply a hypothesis on molecular structure, any more than H^+ implies free protons in the solution or than $NaCl(s)$ implies that this solid is made out of molecules.

on the size of the droplet and on the solute content. Fig. 1 represents these curves for particles of various masses of NaCl. The "pure water" curve is given by the well known Kelvin's equation. If the supersaturation reaches a value of, say, 0.2%, particles of 10^{-15} g or larger will pass over the maxima of the curves and continue growing toward cloud drop size, even after the supersaturation decays (see for instance, Mason, 1971, p.24 ff.).

Thus, for normally attained supersaturations, particles containing 10^{-15} g of soluble material will become activated. Some of these substances may be alkaline, like the sometimes abundant CaCO_3 , that will dissolve in the slightly acidic cloud water, losing CO_2 . For instance, if an activated nucleus contains 10^{-16} g CaCO_3 , by the time the drop reaches 10 μm size, this represents an alkalinity of 5×10^{-7} N. 10^{-15} g CaCO_3 would represent 5×10^{-6} N. By comparison, 1 ppb(v) of NH_3 becoming totally dissolved in a cloud containing $r_L = 5 \times 10^{-3}$ would be equivalent to an alkali concentration of 7×10^{-6} N. This indicates that alkalinity of the aerosol particles may play an important role in determining the final equilibrium (and pH) in cloud water. This rainout effect may concur with washout of alkaline particles to explain observations such as those by Munger (1982).

In the following examples, the aerosol alkalinity has not been taken into account; however, a term indicated Alk has been left in the formulas, as representing alkalinity from this source, so that values different from 0 could be easily introduced.

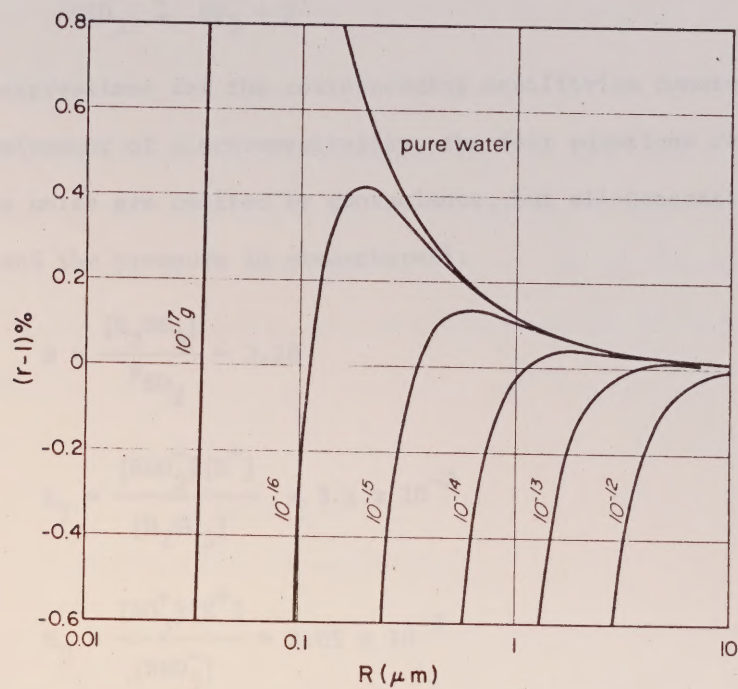
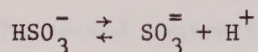
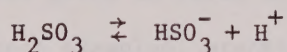
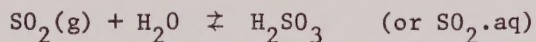


Fig. I.1 — Vapor pressure of NaCl solution drops, as a function of drop radius R . $(r-1)$: supersaturation. Numbers on curves indicate mass of NaCl.

4. SO₂ dissolving in pure water

The equilibria to be considered are the solubility of the gas and the two dissociations of sulfurous acid:



Using the expressions for the corresponding equilibrium constants, and adding the requirement of electroneutrality, the four equations to be considered are (the units are omitted by convenience, but all concentrations are in molarities and the pressure in atmospheres):

$$H = \frac{[\text{H}_2\text{SO}_3]}{p_{\text{SO}_2}} = 3.28$$

$$K_1 = \frac{[\text{HSO}_3^-][\text{H}^+]}{[\text{H}_2\text{SO}_3]} = 3.1 \times 10^{-2}$$

$$K_2 = \frac{[\text{SO}_3^{=}] [\text{H}^+]}{[\text{HSO}_3^-]} = 2.05 \times 10^{-7}$$

$$[\text{HSO}_3^-] + 2[\text{SO}_3^{=}] = [\text{H}^+]$$

The four unknowns are $[\text{H}_2\text{SO}_3]$, $[\text{HSO}_3^-]$, $[\text{SO}_3^{=}]$ and $[\text{H}^+]$. p_{SO_2} is here the independent variable. The equation for $[\text{H}^+] \equiv X$, where X is used for convenience, can be obtained as

$$X^3 - (K_1 H p_{SO_2}) X - 2 K_1 K_2 H p_{SO_2} = 0$$

or

$$X^3 - 1.02 p_{SO_2} X - 4.17 \times 10^{-8} p_{SO_2} = 0$$

Examples of solutions are given in Table 2, for three values of p_{SO_2} .

As it can be seen in these examples, practically all the SO_2 dissolved is in the form of HSO_3^- . The second ionization is in that case negligible, so that $[HSO_3^-] = [H^+] = (K_1 H p_{SO_2})^{1/2}$.

$[HSO_3^-]$ represents almost all the dissolved SO_2 not only for solutions in pure water but also in any solutions (whether or not NH_3 is also present and $Alk \neq 0$), provided the pH is in the range of 3 to 6. As the pH of cloud and rain water is usually in this range, the simplification $[HSO_3^-] \approx [S(IV)]$ is usually applicable.

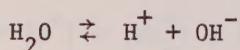
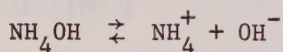
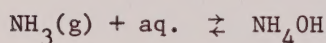
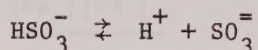
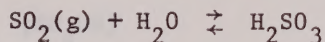
Table 2

(concentrations in molarities)

	$p_{SO_2} = 10^{-9} \text{ atm}$	$p_{SO_2} = 10^{-8} \text{ atm}$	$p_{SO_2} = 2.7 \times 10^{-8} \text{ atm}$
$[H^+]$	1.03×10^{-5}	3.2×10^{-5}	5.24×10^{-5}
pH	4.99	4.49	4.3
$[H_2SO_3]$	3.28×10^{-9}	3.28×10^{-8}	
$[HSO_3^-]$	9.9×10^{-6}	3.2×10^{-5}	
$[SO_3^{=}]$	2.0×10^{-7}	2.0×10^{-7}	

5. System with SO₂, NH₃ and aerosol alkalinity

The equilibria to be taken into account now are:



It is clear that the presence of the ammonia, because it produces OH⁻ ions that combine with H⁺ to give the little dissociated H₂O, thus eliminating H⁺ ions from the equilibrium, cause a general displacement of the three reactions involving SO₂ towards the right. The result is a higher solubilization of SO₂ in the water. Any aerosol alkalinity, also eliminating H⁺ ions, will have a similar effect.

The 7 unknowns are: [H₂SO₃], [HSO₃⁻], [SO₃⁼], [NH₄OH], [NH₄⁺], [H⁺] ≡ X, [OH⁻]. The input parameters are: p_{SO₂}, p_{NH₃}, Alk (alkalinity coming from the aerosol).

The 7 equations are:

$$(1) \quad H = \frac{[\text{H}_2\text{SO}_3]}{p_{\text{SO}_2}}$$

$$(2) \quad K_1 = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]}$$

$$(3) \quad K_2 = \frac{[H^+][SO_3^{=}]}{[HSO_3^-]}$$

$$(4) \quad H_{NH_3} = \frac{[NH_4OH]}{P_{NH_3}}$$

$$(5) \quad K_{NH_3} = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$(6) \quad K_w = [H^+][OH^-]$$

$$(7) \quad Alk + [H^+] + [NH_4^+] = [HSO_3^-] + 2[SO_3^{=}] + [OH^-]$$

The solution of this system is discussed in Appendix A.

6. System with SO_2 and NH_3 in amounts limited to an initial input, and aerosol alkalinity.

The air contains initially (before any solubilization) given concentrations $C_{SO_2, T}$ and $C_{NH_3, T}$. After solubility equilibrium is attained, the air remains with concentrations C_{SO_2} and C_{NH_3} , and the liquid water (r_L) has acquired

$$[S(IV)] \approx [HSO_3^-] + [SO_3^{=}] \quad ([H_2SO_3] \text{ is completely negligible for } pH > 3)$$

and⁽¹⁾

$$[N] \approx [NH_4^+] \quad ([NH_4OH] \ll [NH_4^+] \text{ for } pH < 7)$$

Mass conservation requires

$$C_{SO_2} + 10^{-3} \rho_w^{-1} \mu_{SO_2} r_L [S(IV)] = C_{SO_2,T}$$

$$C_{NH_3} + 10^{-3} \rho_w^{-1} \mu_{NH_3} r_L [NH_4^+] = C_{NH_3,T}$$

$C_{SO_2,T}$ and $C_{NH_3,T}$ (or equivalently, $C_{SO_2,T(V)}$, $C_{NH_3,T(V)}$ and p) are now the initial parameters.

System of equations: (assuming $3 < pH < 7$ and using: $p_{SO_2} = C_{SO_2}(V) p = C_{SO_2} \frac{\mu_a p}{\mu_{SO_2}}$).

(1)

$$\frac{[NH_4OH]}{[NH_4^+]} = \frac{K_w}{K_{NH_3} [H^+]} = \frac{8.3 \times 10^{-11}}{[H^+]}$$

$$\text{For } [H^+] = 10^{-7}, \quad \frac{[NH_4OH]}{[NH_4^+]} = 8.3 \times 10^{-4}$$

$$(1) \quad c_{\text{SO}_2,0} = c_{\text{SO}_2} + k[\text{SO}_2]$$

$$= \left(\frac{\mu_{\text{SO}_2}}{\mu_a p} \right) p_{\text{SO}_2} + k \{ [\text{HSO}_3^-] + [\text{SO}_3^{=}] \} \quad (k = 10^{-3} \rho_w^{-1} \mu_{\text{SO}_2} r_L)$$

$$(2) \quad H = \frac{[\text{H}_2\text{SO}_3]}{p_{\text{SO}_2}}$$

$$(3) \quad K_1 = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]}$$

$$(4) \quad K_2 = \frac{[\text{H}^+][\text{SO}_3^{=}] }{[\text{HSO}_3^-]}$$

$$(5) \quad c_{\text{NH}_3,0} = \left(\frac{\mu_{\text{NH}_3}}{\mu_a p} \right) p_{\text{NH}_3} + k_a [\text{NH}_4^+] \quad (k_a = 10^{-3} \rho_w^{-1} \mu_{\text{NH}_3} r_L)$$

$$(6) \quad H_{\text{NH}_3} = \frac{[\text{NH}_4\text{OH}]}{p_{\text{NH}_3}}$$

$$(7) \quad K_{\text{NH}_3} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

$$(8) \quad K_w = [\text{H}^+][\text{OH}^-]$$

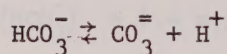
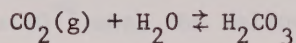
$$(9) \quad \text{Alk} + [\text{H}^+] + [\text{NH}_4^+] = [\text{HSO}_3^-] + 2[\text{SO}_3^{=}] + [\text{OH}^-]$$

9 unknowns: p_{SO_2} or c_{SO_2} , p_{NH_3} or c_{NH_3} , $[\text{H}_2\text{SO}_3]$, $[\text{HSO}_3^-]$, $[\text{SO}_3^{=}]$, $[\text{NH}_4\text{OH}]$, $[\text{NH}_4^+]$, $[\text{H}^+]$, $[\text{OH}^-]$.

The solution of this system is discussed in Appendix B.

7. Equilibrium of CO₂

CO₂ is always present in the atmosphere, in a constant concentration of about 330 ppm(V). Its solubility and dissociation equilibria



must be considered, and their influence on the SO₂ equilibria must be examined. The equilibrium on pure water will first be examined in this section.

The following values for the constants may be used:

Table 3 - Constants for CO₂

	T: 25°C	10°C	0°C
$K_{1,\text{CO}_2} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}$	4.4×10^{-7}	3.4×10^{-7}	2.64×10^{-7}
$K_{2,\text{CO}_2} = \frac{[\text{CO}_3^{=}] [\text{H}^+]}{[\text{HCO}_3^-]}$	5.6×10^{-11}	3.2×10^{-11}	$\sim 2 \times 10^{-11}$ (by extrapolation)
$H_{\text{CO}_2} = \frac{[\text{H}_2\text{CO}_3]}{p_{\text{CO}_2}}$	0.0339	5.33×10^{-2}	0.076

(As always, concentrations in M, p_{CO_2} in atm).

The study of the equilibrium at 10°C ($K_w = 3.0 \times 10^{-15} \text{ M}^2$), using the constants above written and the neutrality equation

$$[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{=}]$$

gives, for $p_{\text{CO}_2} = 3 \times 10^{-4} \text{ atm}$, the following set of concentrations:

$$[\text{H}_2\text{CO}_3] = 1.6 \times 10^{-5} \text{ M}$$

$$[\text{HCO}_3^-] = 2.4 \times 10^{-6} \text{ M}$$

$$[\text{CO}_3^{=}] = 3.2 \times 10^{-11} \text{ M}$$

$$[\text{H}^+] = 2.3 \times 10^{-6} ; \text{ pH} = 5.6$$

If the ratios among the dissolved species are considered for varying pH, the following values are readily found for 0°C:

pH:	3	4	6
$[\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$	2.64×10^{-4}	2.64×10^{-3}	2.64×10^{-1}
$[\text{CO}_3^{=}]/[\text{HCO}_3^-]$	-	-	2×10^{-5}

It is clear that the second dissociation can be ignored for the whole range of pH, and that

$$[\text{C(IV)}] \approx [\text{H}_2\text{CO}_3] \quad \text{for } \text{pH} < 4$$

$$[\text{C(IV)}] \approx [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] \quad \text{for } 4 < \text{pH} < 6$$

8. System with SO_2 and NH_3 in amounts limited to an initial input, CO_2 and aerosol alkalinity.

The concentration of CO_2 in the air is so high (330 ppm(V)) that it may be taken as a constant, and the dissolved concentration will also be a constant, provided the temperature is assumed constant.

To the system of equations of p. 17, one should add the 3 expressions of HCO_2 , K_{1,CO_2} , and K_{2,CO_2} . 3 new unknowns appear: $[\text{H}_2\text{CO}_3]$, $[\text{HCO}_3^-]$ and $[\text{CO}_3^{=}]$. And the electroneutrality must now be written

$$\text{Alk} + [\text{H}^+] + [\text{NH}_4^+] = [\text{HSO}_3^-] + 2[\text{SO}_3^{=}] + [\text{HCO}_3^-] + 2[\text{CO}_3^{=}] + [\text{OH}^-]$$

However, it has been shown in the previous section that the second ionization can be ignored (and so can $[\text{CO}_3^{=}]$ in the neutrality equation) and the equation of Henry's law can be readily eliminated, as p_{CO_2} is a constant and $[\text{H}_2\text{CO}_3]$ only depends on it.

The system becomes one of 7 equations:

$$(11) \quad C_{\text{SO}_2,0} = k^1 [\text{H}_2\text{SO}_3] + k [\text{HSO}_3^-] + [\text{SO}_3^{=}]$$

$$(12) \quad K_1 = \frac{[\text{H}^+] [\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]}$$

$$(13) \quad K_2 = \frac{[\text{H}^+] [\text{SO}_3^{=}]}{[\text{HSO}_3^-]}$$

$$(14) \quad C_{\text{NH}_3,0} = k_a^1 [\text{NH}_4\text{OH}] + k_a [\text{NH}_4^+]$$

$$(15) \quad K_{\text{NH}_3} = \frac{[\text{NH}_4^+] K_w}{[\text{NH}_4\text{OH}] [\text{H}^+]}$$

$$(20) \quad K_{1,\text{CO}_2} = \frac{[\text{HCO}_3^-] [\text{H}^+]}{[\text{H}_2\text{CO}_3]}$$

$$(21) \quad \text{Alk} + [\text{H}^+] + [\text{NH}_4^+] = [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-]$$

where $k = 10^{-3} \rho_w^{-1} \mu_{\text{SO}_2} r_L = 0.064 r_L$, $k^I = \frac{\mu_{\text{SO}_2}}{\mu_a^{\text{pH}}}$

$$k_a = 10^{-3} \rho_3^{-1} \mu_{\text{NH}_3} r_L = 0.017 r_L, \quad k_a^I = \frac{\mu_{\text{NH}_3}}{\mu_a^{\text{pH}_{\text{NH}_3}}}$$

There are 7 unknowns: $[\text{H}_2\text{SO}_3]$, $[\text{HSO}_3^-]$, $[\text{SO}_3^{2-}]$, $[\text{NH}_4\text{OH}]$, $[\text{NH}_4^+]$, $[\text{HCO}_3^-]$, $[\text{OH}^-]$. Formulas (17)-(19) (App. B) are valid as before, and HCO_3^- is given by

$$[\text{HCO}_3^-] = \frac{K_{1,\text{CO}_2} [\text{H}_2\text{CO}_3]}{[\text{H}^+]} \quad (22)$$

The solution of this system is considered in Appendix C.

9. Examples of solution for the system with SO_2 and NH_3 in amounts limited to an initial input, without and with CO_2 . No aerosol alkalinity ($\text{Alk}=0$).

The systems of equations of sections 6 and 8 were solved for a number of examples. In all of them the following values were used:

$$p = 0.6 \text{ atm}$$

$$T = 0^\circ\text{C}$$

$$r_L = 5 \times 10^{-3}$$

$$\text{Alk} = 0$$

$$p_{\text{CO}_2}/p = 3.3 \times 10^{-4}$$

and accordingly, the following constants were used:

$$k = 3.2 \times 10^{-4} \text{ M}^{-1}$$

$$k' = 1.123 \text{ M}^{-1}$$

$$k_a = 8.5 \times 10^{-5} \text{ M}^{-1}$$

$$k'_a = 4.25 \times 10^{-2} \text{ M}^{-1}$$

$$[\text{H}_2\text{CO}_3] = 1.50 \times 10^{-5} \text{ M}$$

The results of the computations for 10 examples without CO_2 and 5 examples with CO_2 are collected in Table 4 and represented in Fig. 2 as a function of the initial concentration of NH_3 in ppb(V) ($C_{\text{NH}_3, T(V)} = \text{ppb(V)} \times 10^{-9}$) and for 3 initial concentrations of SO_2 : 2, 10 and 50 ppb(V) ($C_{\text{SO}_2, T(V)}: 2 \times 10^{-9}, 10^{-8}$ and 5×10^{-8}). The values plotted are the fraction of SO_2 that becomes dissolved, and the equilibrium pH. The solutions of the equations also provide, of course, the values for all the concentrations of the different species in solution and the remaining concentrations of

Table 4
Summary of Examples

No CO ₂ present						CO ₂ present		
Example	Initial concentration of SO ₂ in ppb(V)	Initial concentration of NH ₃ in ppb(V)	Molar ratio $\frac{P_{NH_3}}{P_{SO_2}}$	pH	Fraction dissolved	Example	pH	Fraction dissolved
1	50	10	0.2	4.61	0.26	1'	4.61	0.27
2	50	0	0	4.29	0.15	-	-	-
3	10	10	1	5.85	0.88	3'	5.79	0.86
4	10	0	0	4.68	0.30	4'	4.68	0.30
5	50	5	0.1	4.45	0.20	-	-	-
6	10	5	0.5	5.17	0.58	-	-	-
7	2	0	0	5.11	0.54	7'	5.10	0.53
8	2	10	5	7.60	1.00	-	-	-
9	2	5	2.5	7.47	1.00	-	-	-
10	2	2	1	5.95	0.90	10'	5.75	0.85

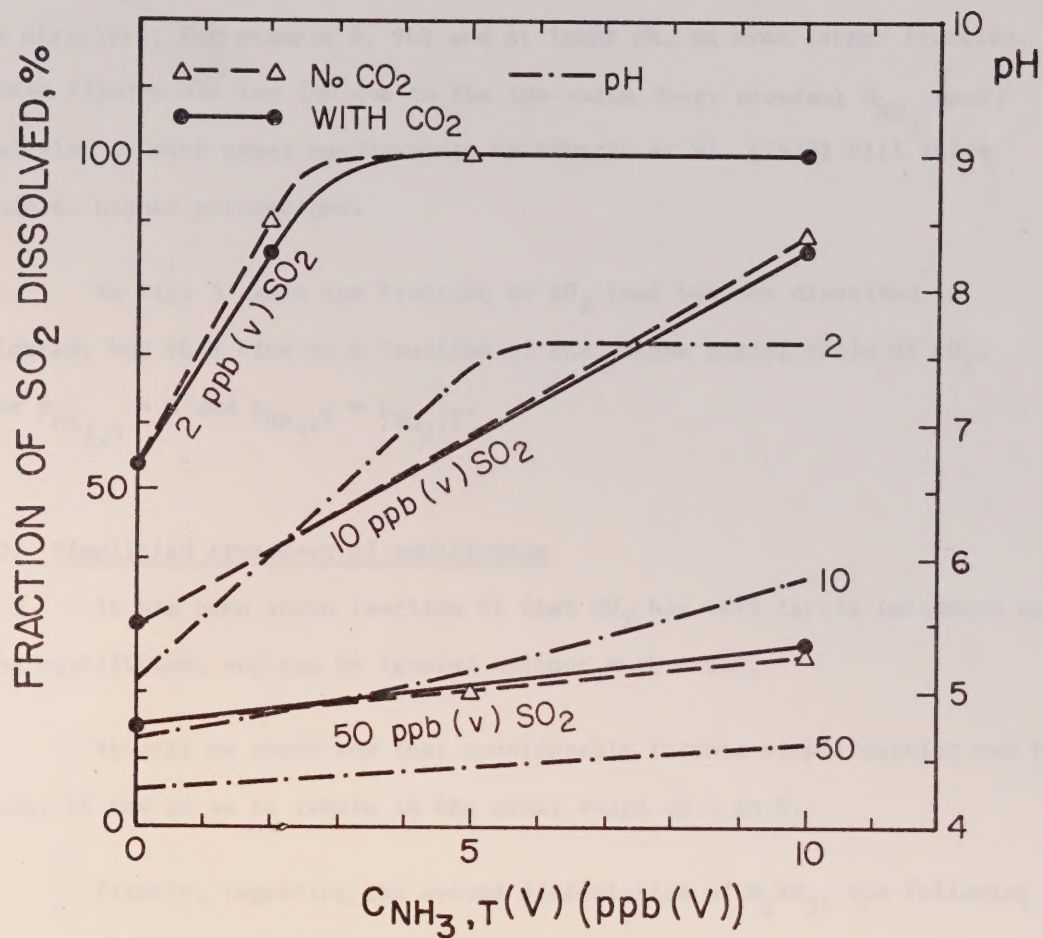


Fig. I.2 - Fraction of SO_2 dissolved in cloud water and resulting pH, as functions of the total initial concentration of NH_3 .

SO_2 and NH_3 in the air.

For all the range of pH in these examples, the concentration of NH_3 dissolved is practically given by $[\text{NH}_4^+]$. Computation shows that almost all the NH_3 becomes dissolved, except for example 8 and 9. For example 8, 57% is dissolved; for example 9, 96% and at lower pH, an even larger fraction. These figures are too low due to the low value Henry constant H_{NH_3} used; calculation with newer measurements by Edwards et al. (1975) will raise them to higher percentages.

In Fig. 3 again the fraction of SO_2 that becomes dissolved is plotted, but this time as a function of the volume mixing ratio of SO_2 , for $p_{\text{NH}_3,0} = 0$ and $p_{\text{NH}_3,T} = p_{\text{SO}_2,T}$.

10. Simplified treatment of equilibrium

It has been shown (section 9) that CO_2 has very little influence on the equilibrium, and can be ignored without much error.

It will be shown now that considerable further simplification can be made, if the pH is to remain in the usual range of 3 to 6.

Firstly, regarding the second dissociation of H_2SO_3 , the following values can be calculated:

	pH = 3	pH = 6	
$\frac{[\text{SO}_3^{=}]}{[\text{HSO}_3^-]} = \frac{K_2}{[\text{H}^+]}$:	2×10^{-4}	2×10^{-1}	at 0°C
	6×10^{-5}	6×10^{-2}	at 25°C

Only at the highest pH this dissociation starts being appreciable. As a

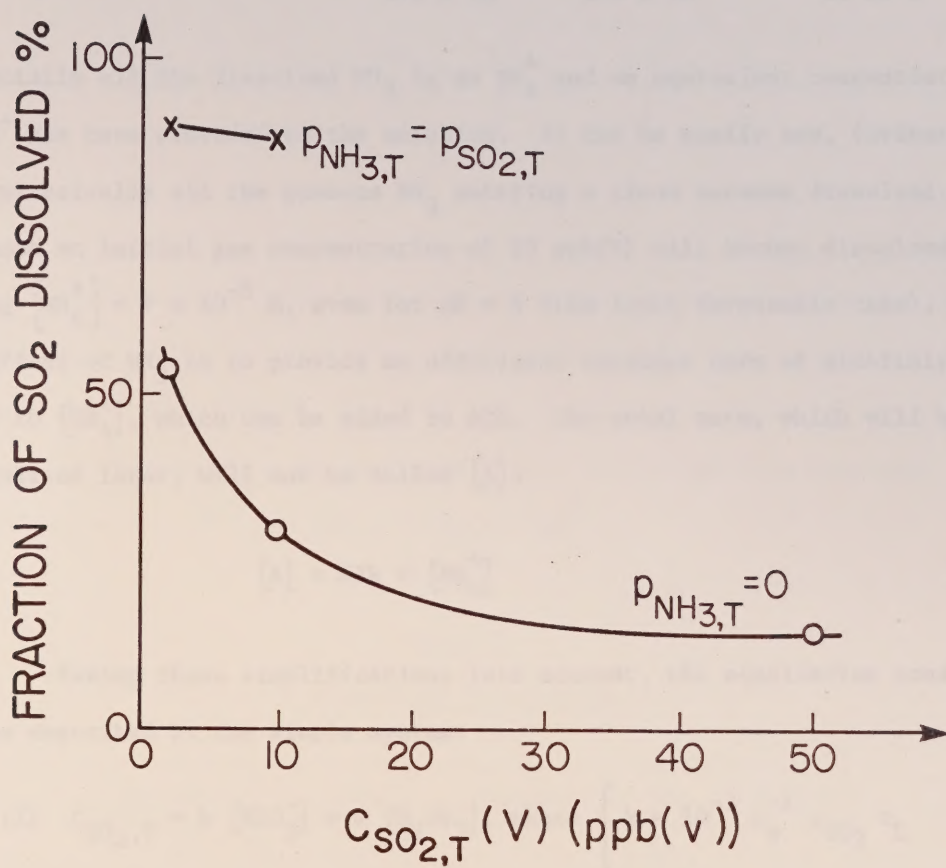


Fig. I.3 - Fraction of SO_2 dissolved in cloud water, for $p_{\text{NH}_3} = 0$

and $p_{\text{NH}_3} = p_{\text{SO}_2}$.

reasonable approximation, it can be ignored over the whole range of pH. It may also be noticed that in this range, $|S(IV)| \approx |HSO_3^-|$, i.e., practically all the dissolved SO_2 is in the form of HSO_3^- .

Secondly, a similar calculation shows that for NH_3 :

$\frac{[NH_4^+]}{[NH_4OH]} = \frac{K_{NH_3} [H^+]}{K_w} :$	pH = 3	pH = 6	
	1.2×10^7	1.2×10^4	at 0°C
	1.8×10^7	1.8×10^4	at 25°C

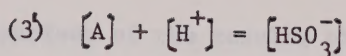
Essentially all the dissolved NH_3 is as NH_4^+ and an equivalent concentration of OH^- has been provided to the solution. It can be easily see, furthermore, that practically all the gaseous NH_3 entering a cloud becomes dissolved. For instance an initial gas concentration of 10 ppb(V) will become dissolved, giving $[NH_4^+] = 7 \times 10^{-5}$ M, even for pH = 6 (the least favourable case). Thus the effect of NH_3 is to provide an additional constant term of alkalinity, equal to $[NH_4^+]$, which can be added to Alk. The total term, which will be generalized later, will now be called [A]:

$$[A] = Alk + [NH_4^+] \quad (24)$$

Taking these simplifications into account, the equilibrium conditions become described by the simple system:

$$(1') \quad C_{SO_2,T} = k [HSO_3^-] + k' [H_2SO_3], \text{ where } \begin{cases} k = 10^{-3} \rho_w^{-1} \mu_{SO_2} r_L \\ k' = \frac{\mu_{SO_2}}{\mu_a H p} \end{cases}$$

$$(2') \quad K_1 = \frac{[HSO_3^-] [H^+]}{[H_2SO_3]}$$



where (1') joins the condition of mass conservation and Henry's law. Solution of this system leads to the second degree equation

$$x^2 + \left([A] + \frac{kK_1}{k'}\right)x + \frac{K_1}{k'}(k[A] - C_{SO_2,T}) = 0 \quad (25)$$

where $x \equiv [H^+]$ has been written for simplicity. Therefore

$$x \equiv [H^+] = -\frac{1}{2} \left([A] + \frac{kK_1}{k'}\right) + \sqrt{\frac{1}{4} \left([A] + \frac{kK_1}{k'}\right)^2 - \frac{K_1}{k'}(k[A] - C_{SO_2,T})} \quad (26)$$

Application of this simplified treatment to several examples yields the results of Table 5. Here the examples 1'', 2'', 4'', etc. correspond to the examples 1 and 1', 2 and 2', 4 and 4', etc. in Table 4, regarding the concentrations of SO_2 and NH_3 . As for Table 4, the calculation has been done for $T = 0^\circ C$, $r_L = 5 \times 10^{-3}$ and $Alk = 0$ ($[A] = [NH_4^+]$).

Table 5
Simplified Calculation

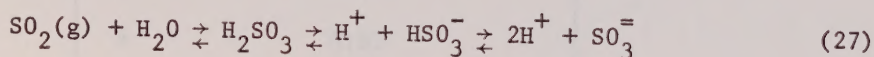
Example	pH	Fraction of SO_2 dissolved
1''	4.67	0.26
2''	4.32	0.14
4''	4.71	0.28
6''	5.26	0.58
7''	5.15	0.52

Comparison of the results of Table 5 with those of Table 4 shows that the approximation is quite satisfactory.

This approximation breaks down for $C_{\text{NH}_3, \text{T}}(\text{V}) \geq C_{\text{SO}_2, \text{T}}(\text{V})$.

11. The effect of acidity on the distribution of SO_2 between the two phases.

In the chain of equilibria



it is clear that higher values of $[\text{H}^+]$ will tend to displace the reactions toward the left (and vice versa). If this occurs in a closed system, the position of the equilibrium will determine the fraction of SO_2 that resides in the liquid. A cloud parcel must be considered as a closed system, either because it is assumed large enough to neglect mixing at the borders, or because it may be argued that the environment (if the parcel is small) has the same properties.

The fraction dissolved can be readily obtained from

$$C_{\text{SO}_2, \text{T}} = C_{\text{SO}_2} \left(1 + 10^{-3} \rho_w^{-1} \mu_a r_L \frac{K_1 H}{[\text{H}^+]} p \right) \quad (28)$$

which condenses the conditions of mass conservation and Henry's law. Here the first term at the right is the part remaining in gas phase, while the second one gives the part dissolved in cloud water. Thus the fraction dissolved is

$$\frac{10^{-3} \rho_w^{-1} \mu_a r_L K_1 H p / [\text{H}^+]}{1 + 10^{-3} \rho_w^{-1} \mu_a r_L K_1 H p / [\text{H}^+]} \quad (29)$$

It is clear that this fraction must decrease with increasing $[H^+]$. As an example, the fraction has been calculated for 0°C ($K_1 = 3.1 \times 10^{-2} \text{ M}$; $H = 2.86 \text{ M atm}^{-1}$), $r_L = 5 \times 10^{-3}$ and $p = 0.6 \text{ atm.}$, and varying pH. The results are illustrated by Table 6 and Fig. 4.

Table 6

pH	Fraction of SO_2 dissolved
3	0.01
4	0.07
5	0.44
6	0.89

It is clear that a value of pH around 3 may put a virtual limit for reaction rates proportional to $[\text{HSO}_3^-]$.

12. Conclusions

From the analysis performed in this chapter, the following points may be concluded:

1. NH_3 has a very important effect on the solubilization of SO_2 , and therefore it may affect considerably its rate of oxidation in liquid phase. This effect becomes obvious from the observation of Figs. 2 and 3. The range of concentrations tested is well within the range observed, as well for the NH_3 (for instance, 0.1 to 30 ppb(V), according to Harward et al. (1982)), as for SO_2 .
2. The aerosol, if alkaline, may also have considerable effect. To

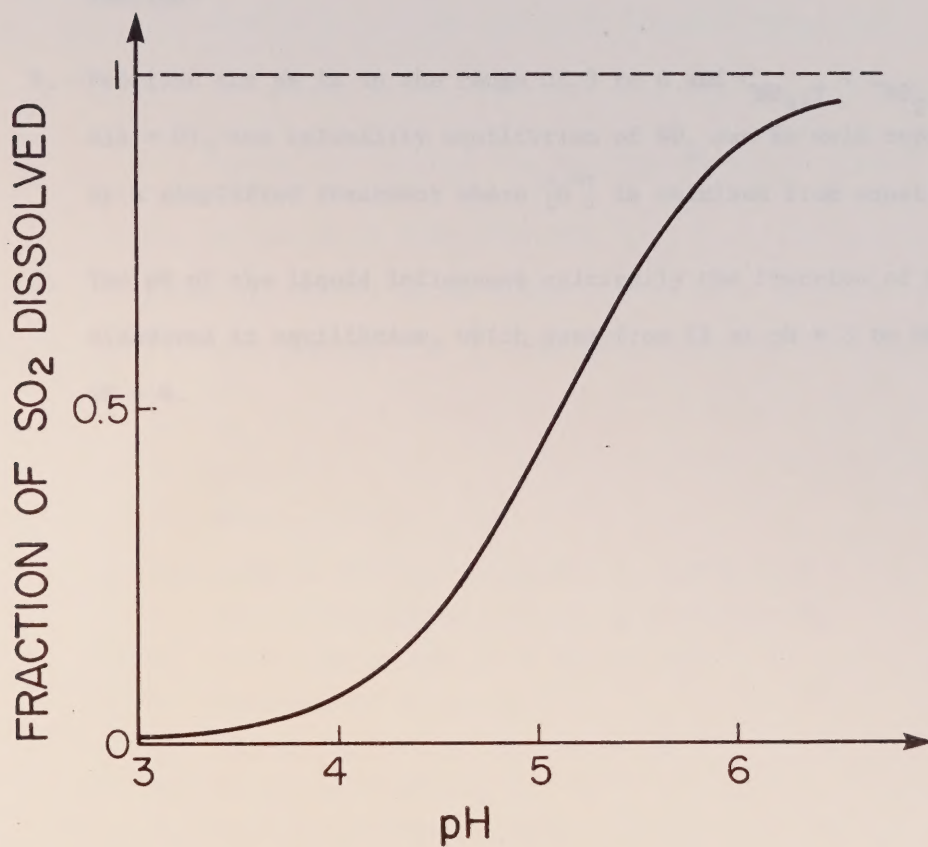


Fig. I.4 - Fraction of SO_2 dissolved in cloud water as a function of pH.

assess properly this effect, however, knowledge of the alkali concentration produced in cloud droplets (the term Alk in the equation) would be required; obviously this is not an easy estimate to make.

3. CO_2 has a comparatively large concentration in the atmosphere but a low solubility. Its effect on the equilibria has been shown to be insignificant, so that its presence can be ignored in a first approximation.
4. Provided the pH is in the range of 3 to 6 and $C_{\text{NH}_3, \text{T}} < C_{\text{SO}_2, \text{T}}$ (for $\text{Alk} = 0$), the solubility equilibrium of SO_2 can be well represented by a simplified treatment where $[\text{H}^+]$ is obtained from equation (26).
5. The pH of the liquid influences critically the fraction of SO_2 dissolved in equilibrium, which goes from 1% at $\text{pH} = 3$ to 89% at $\text{pH} = 6$.

II. IN-CLOUD CHEMISTRY

A. INTRODUCTION

B. OXIDATION OF SO_2 AND REDUCED S COMPOUNDS IN CLOUD WATER

1. Oxidation by H_2O_2
2. Oxidation by O_3
3. Oxidation by O_2
4. Catalyzed oxidation
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6. Oxidation by oxo compounds of nitrogen
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C. OXIDATION OF SO_2 IN GAS PHASE

D. IN-CLOUD CHEMISTRY OF N COMPOUNDS. SOLUBILITY OF N OXO COMPOUNDS

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2. NO_2
3. HNO_2
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E. REACTIONS OF NITROGEN COMPOUNDS IN LIQUID PHASE

1. Disproportionation reaction of dissolved NO_2
2. Production of HNO_2 from NO and NO_2
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8. Reduction of HNO_2 by SO_2

F. REACTIONS OF NITROGEN COMPOUNDS IN GAS PHASE

1. Production of HNO_3
2. Production of HNO_2

G. SUMMARY FOR N OXO COMPOUNDS

A. INTRODUCTION

In this chapter, the chemistry of sulfur and nitrogen compounds is examined. Only the main facts significant to this study are extracted from the literature; no attempt is made to give a summary covering all aspects of this complex field. For instance, in the sections referring to gas phase, the only point that has been considered is whether the relaxation times for reactions in gas phase are long enough, when compared with the cloud droplets life times, to justify neglecting consideration of these reactions.

The bibliography dedicated to the relevant subjects is very abundant. This survey has been greatly facilitated by recent review papers, which permitted a rapid location of the original publications, and in some cases were explicit enough to obtain the desired conclusions without the need for consulting the original sources. Extensive use has been made in particular of:

Graedel and Weschler, 1981, which will hereafter be abbreviated by GW

Chameides and Davis, 1982, which will hereafter be abbreviated by CD

The following summaries were also consulted:

Möller, 1980

Graedel, 1979

Ogram, 1982.

The appraisal of the possible importance of various reactions has been made by approximate computations, based on typical values of the concentrations of the chemical species involved, and on the values of constants found in the literature. Regarding these last values, it may be remarked that most of them are given for 25°C or similar temperatures, which are certainly not typical of the in-cloud conditions; values at 0°C are scarce and values for supercooled water are nonexistent. This, however, is not important for the present order-of-magnitude estimates.

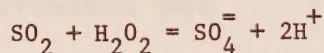
A more important remark must be made regarding the way in which these estimates are made. It is frequent to find arguments such as: "considering that the air may contain 1 ppb(v) of H_2O_2 and that the Henry coefficient is 10^5 M atm^{-1} , the concentration in the droplets may be assumed to be (assuming 1 atm total pressure for simplicity) 10^{-4} M ; etc.". This simplistic argument disregards the fact that the H_2O_2 dissolved in the cloud water cannot be replaced during the process in question, so that the actual gaseous concentration in equilibrium with the water phase will be lower. In the present estimates the requirements of mass conservation for the species involved has always been taken into account.

When assessing the possible importance of a reaction, it is frequently concluded that its rate "is negligible". This is meant to indicate that the reaction rate is insufficient to contribute in any appreciable degree to the transformation of the species considered (e.g. SO_2) during the life times of liquid water in clouds.

For simplicity, subscripts indicating the chemical species to which various constants refer have been omitted, when no ambiguity could result.

B. OXIDATION OF SO_2 AND REDUCED S COMPOUNDS IN CLOUD WATER

1. Oxidation by H_2O_2



Martin and Damschen (1981) studied the oxidation of dissolved SO_2 in water by H_2O_2 and found that its rate was given by

$$v = \frac{d[\text{S (IV)}]}{dt} = \frac{(8 \pm 2) \times 10^4 [\text{H}_2\text{O}_2][\text{SO}_2.\text{aq}]}{0.1 + [\text{H}^+]} \text{ M s}^{-1}$$

within $0 < \text{pH} < 5$, at 25°C . For the range of pH of interest (3-6), $[\text{H}^+]$ is negligible in the denominator, and the expression becomes

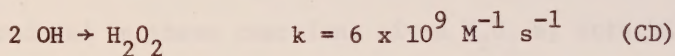
$$v = 8 \times 10^5 [\text{H}_2\text{O}_2] [\text{H}_2\text{SO}_3] \text{ M s}^{-1}$$

If we want the expression in terms of $[\text{HSO}_3^-]$, which is approximately equal to the total SO_2 dissolved in that range of pH of our interest,

$$\begin{aligned} v &= 5.2 \times 10^7 [\text{H}_2\text{O}_2] [\text{HSO}_3^-] [\text{H}^+] \\ &= 5.2 \times 10^7 [\text{H}_2\text{O}_2] [\text{H}^+] [\text{S(IV)}] \end{aligned}$$

The numerical constant is given for 25°C. An appreciably different value is to be expected at, say, 0°C. In these expressions, $[\text{H}_2\text{SO}_3]$ or $[\text{HSO}_3^-]$ and $[\text{H}^+]$ will depend on the inflow concentrations of SO_2 and NH_3 (and eventually on the alkalinity of the aerosol, as studied with respect to the equilibrium conditions). We also need to know $[\text{H}_2\text{O}_2]$, i.e. the concentration of H_2O_2 in the liquids. H_2O_2 comes in the inflowing air, in concentrations of 0.1 - 10 ppb(v) (Harward et al., 1982; GW). The coefficient of Henry's law is 1×10^5 at 25°C, so that the corresponding equilibrium concentration in water, at 1 atm, would be 10^{-5} to 10^{-3} M. However, if the gaseous H_2O_2 is depleted by dissolution, the concentration in the liquid will not reach that value. One should also consider the magnitude of the sources and sinks of H_2O_2 both in gas and liquid phases.

One of the sources in the liquid is

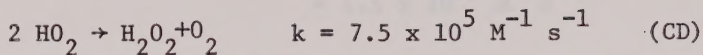


corresponding to a production rate

$$v_p = k [\text{OH}]^2$$

$[\text{OH}]$ can be estimated in a cloud to be in the range 3×10^{-14} to 2×10^{-12} M (CD, p. 4869). The highest value will give $v_p = 2.4 \times 10^{-14} \text{ M s}^{-1} = 9 \times 10^{-11} \text{ M hr}^{-1}$, which is entirely negligible.

Another source is

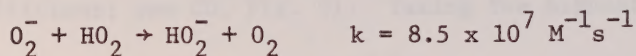


corresponding to

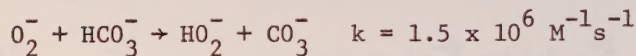
$$v_p = k [\text{HO}_2]^2$$

$[\text{HO}_2]$ can be estimated to be in the range 10^{-9} to 10^{-8} M (CD, p. 4873, Fig.7; also, their Table 5). Taking the highest value, $v_p = 7.5 \times 10^{-11} \text{ M s}^{-1} = 3 \times 10^{-7} \text{ M hr}^{-1}$, again negligible.

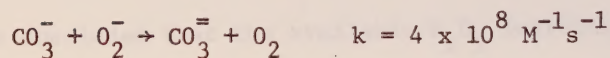
However, the most important source is provided by the reactions



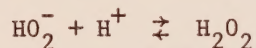
and



followed by

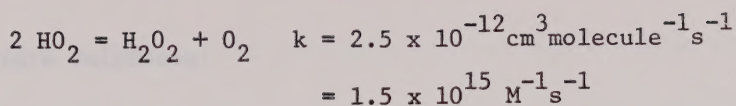


The species HO_2^- produced in these reactions gives H_2O_2 by attaching a proton:



CD estimate the resulting rate of production in liquid phase (see their Table 6) in $8.2 \times 10^{-6} \text{ M hr}^{-1} = 1.4 \times 10^{-7} \text{ M min}^{-1}$.

It remains to be seen whether the rate of replacement of gaseous H_2O_2 can be appreciable in replacing the H_2O_2 dissolved. The source is the reaction



(R.D. Hudson (ed.) - Chlorofluoromethanes and the stratosphere, NASA Ref.

Publ. 1010, 1977. Cited by Graedel, 1979, Table 2). Gaseous concentrations of HO_2 are in the range $10^{-4} - 10^{-1}$ ppb(v), with typical value 10^{-2} ppb(v) (Logan, 1981) or $10^8 - 10^9 \text{ cm}^{-3}$ in cloud free conditions (CD), equivalent at 1 atm to 0.004 to 0.04 ppb(v) (CD, p.4866). However, in a cloud the HO_2 molecules are lost to the droplets, while their production should also be reduced by the reduction in photochemistry and the range of concentration is estimated in 2×10^6 to 10^8 cm^{-3} (according to the values of cloud transmissivity and accommodation coefficient; see CD, Fig. 3). Taking the highest value, the maximum production rate can be estimated by

$$k[\text{HO}_2]^2 = 2.5 \times 10^{-12} \times (10^8)^2 = 2.5 \times 10^4 \text{ cm}^{-3} \text{ s}^{-1}$$

equivalent to $10^{-15} \text{ atm s}^{-1}$, or, at 1 atm, to $10^{-6} \text{ ppb(v) s}^{-1}$. Therefore entirely negligible.

It can be concluded that the available H_2O_2 introduced into the cloud by air inflow is not to be replaced once depleted, except in the estimated rate of production in the liquid $8.2 \times 10^{-6} \text{ M hr}^{-1}$ mentioned above.

Thus, it is assumed that dissolution equilibrium is established rapidly enough (and not considering chemical reaction for the moment), one must obtain H_2O_2 (in the liquid) from the two equations:

$$C_{\text{dissolved}} + C_{\text{gas phase}} = C_T \quad \text{mass conservation}$$

$$[\text{H}_2\text{O}_2] = H C (v)p \quad \text{Henry}$$

Using the appropriate relations:

$$10^{-3} \rho_w^{-1} \mu_a r_L [\text{H}_2\text{O}_2] + C(v) = C_T(v)$$

$$[\text{H}_2\text{O}_2] = H C(v) p$$

where the symbols have the meanings explained in "Thermodynamic and chemical variables".

Solution:

$$[\text{H}_2\text{O}_2] = \frac{1}{10^{-3} \rho_w^{-1} \mu_a r_L + \frac{1}{H}} C_T(v)$$

$$C(v) = [\text{H}_2\text{O}_2] / H$$

Example:

$$r_L = 5 \times 10^{-3}, K \sim 10^5 \frac{\text{M}}{\text{atm}} \text{ (approximated by } 25^\circ\text{C value),}$$

$$C_T(v) = 10^{-9} \text{ (1 ppb(v))}$$

$$[\text{H}_2\text{O}_2] = 6 \times 10^{-6} \text{ M}$$

$$C(v) = 6 \times 10^{-11} \text{ (0.06 ppb (v))}$$

One can see that practically all the inflowing gaseous H_2O_2 becomes dissolved in the cloud water formed by condensation in the same air, and could be estimated simply by

$$[\text{H}_2\text{O}_2] = \frac{C_T(v)}{29 (10^{-3} r_L)}$$

where $C_T(v)$ is the inflowing volume ratio (e.g. 10^{-9} for 1 ppb(v)) and $(10^{-3} r_L) \times 10^6$ is the mass of cloud water, in g per kg of air. It is worth mentioning that recent measurements of H_2O_2 in rainwater by Zika et al. (1982) have given values in the range $(1-7) \times 10^{-5} \text{M}$, and the authors suggest that a substantial fraction of that H_2O_2 may be generated in the cloud water.

Assuming 10^{-5}M to be a typical concentration, it can be introduced in the expression for the rate of oxidation.

Example:

$$\text{Assume } \left[\begin{array}{l} [\text{S(IV)}] = 10^{-5} \text{M} \\ [\text{H}^+] = 10^{-5} \text{M} \end{array} \right] \quad [\text{H}_2\text{O}_2] = 10^{-5} \text{M}$$

$$v = 5.2 \times 10^7 [\text{H}_2\text{O}_2] [\text{H}^+] [\text{S(IV)}]$$

$$= 5.2 \times 10^7 \times 10^{-5} \times 10^{-5} \times 10^{-5} = 5.2 \times 10^{-8} \text{ Ms}^{-1}$$

$$= 3 \times 10^{-6} \text{ M min}^{-1}$$

i.e., the initial rate, starting with these concentrations,

will mean 30% of SO_2 oxidized per minute.

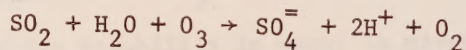
$$\text{If } [\text{H}^+] = 10^{-6} \text{M}, v = 3 \times 10^{-7} \text{ M min}^{-1}$$

From the previous example it is seen that continued production of H_2O_2 in liquid phase, as described before, will only become important at $\text{pH} > 5$. At $\text{pH} = 5$ it is only a minor contribution initially; however, as H_2O_2 becomes depleted by the oxidation of SO_2 , the continued production of H_2O_2 will determine the rate at which oxidation will still proceed ($1.4 \times 10^{-7} \text{ M min}^{-1}$ in the present estimates).

When considering higher rates of oxidation, one may in first approximation ignore the path involving production of H_2O_2 in liquid phase. In that case, the rate equation should be integrated if one wants to calculate the number of moles oxidized in time Δt . An example of this integration is given in Appendix D, under the assumption that SO_2 , as well as H_2O_2 , is not replenished (e.g. by more dissolution from the air) in the liquid phase. The solution is readily attainable, but the resulting formula is too complicated to be used for the present purposes. The reaction proceeds as a complex exponential function of Δt .

2. Oxidation by O_3

The overall reaction is



Two possible mechanisms have been suggested. Erikson et al. (1977) assumed that O_3 could oxidize directly the three species $\text{SO}_3^{=2-}$, HSO_3^{-} , H_2SO_3 , but that the oxidation of the first one is the fastest, so that the reaction occurs at a rate

$$v = k[O_3][SO_3^{\equiv}] = (k K_2)[O_3][HSO_3^-][H^+]^{-1}$$

$$\cong (k K_2)[S(IV)][H^+]^{-1}[O_3]$$

where K_2 is the second dissociation constant and the last equality is valid in the pH range of interest.

Penkett et al. (1979) and Maahs (1982) suggest that the reaction starts with oxidation of OH^- by O_3 to produce HO . Penkett et al. derive the kinetic formula

$$v = k[O_3][HSO_3^-][H^+]^{-\frac{1}{2}}$$

$$\cong k[O_3][S(IV)][H^+]^{-\frac{1}{2}}$$

Their experiments confirm approximately this expression, with a value of k that varies from 7.1×10^3 at $pH = 0$ to 3.6×10^3 at $pH = 7$. However, their own results are better represented by

$$v = k[O_3][HSO_3^-][H^+]^{-0.4}$$

with $k = 1.79 \times 10^4 \text{ M}^{-0.6} \text{ s}^{-1}$ over the whole range of pH.

The concentration of O_3 in the air may be in the range of 10 to 100 ppb(v), and its solubility in water is given by the Henry coefficient $1.3 \times 10^{-2} \text{ M atm}^{-1}$ (at 25°C). Taking 50 ppb(v) as a typical value in the gas, $[O_3] = 6.5 \times 10^{-10} \text{ M}$ (25°C , 1 atm) is the equilibrium concentration in water. We set up the system of equations:

$$10^{-3} \rho_w^{-1} \mu_a r_L [O_3] + C(v) = C_T(v) \quad \text{mass concentration}$$

$$[O_3] = H_{O_3} C(v) p \quad \text{Henry's law}$$

In solving this system it is easily seen that (for the conditions above mentioned) only a fraction of the order of 10^{-6} of the O_3 becomes dissolved, and therefore the concentration in gas phase can be taken as constant ($C(v) \approx C_T(v) = 50 \text{ ppb}(v)$). This situation contrasts with that of H_2O_2 .

For illustration, the last equation is applied to an example with the previous concentration of O_3 :

Example:

$$[O_3] = 6.5 \times 10^{-10} M$$

$$[HSO_3^-] = 10^{-5} M$$

$$[H^+] = 10^{-5} M$$

$$v = 1.79 \times 10^4 \times 6.5 \times 10^{-10} \times 10^{-5} \times (10^{-5})^{-0.4}$$

$$= 1.2 \times 10^{-8} M s^{-1} = 7 \times 10^{-7} M \text{ min}^{-1}$$

$$\text{If } [H^+] = 10^{-6} M, v = 3 \times 10^{-8} M s^{-1} = 1.8 \times 10^{-6} M \text{ min}^{-1}$$

Integration over time might be performed as for H_2O_2 . In this case one would have



$$\text{conc.} \begin{cases} \text{initial} & a & b & 0 & c \\ \text{at } t & a-x & b-x \approx b & x & c+2x \end{cases}$$

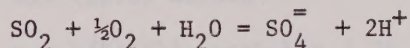
and the equation to integrate would be

$$v = kb (a-x)(c+2x)^{-0.4}$$

The integration might be performed numerically.

3. Oxidation by O_2

The overall reaction is



This oxidation has been studied by a number of authors (Beilke et al., 1975; Scott and Hobbs, 1967; Möller, 1980). Beilke et al. compared the results of previous work and of their own. They found that the oxidation rate could be expressed by

$$v = Q' [SO_3^{=2-}] = Q p_{SO_2}$$

where Q and Q' are functions of $[H^+]$ involving a number of constants (see their Fig. 5 and eqs. (17)-(18)). Considerable uncertainty exists for the values of Q above $pH = 6$. However, in the range $3 < pH < 6$ in which lies the main interest, Q' might be taken as $1.2 \times 10^{-4} [H^+]^{-0.16}$ (although MacKay's (1971) results would give from 1 to 3 orders of magnitude larger values). Then the oxidation rate might be written

$$\begin{aligned} v &= 1.2 \times 10^{-4} [H^+]^{-0.16} [SO_3^{=2-}] \\ &= 1.2 \times 10^{-4} K_1 K_2^H [H^+]^{-2.16} \cdot p_{SO_2} \\ &= 1.6 \times 10^{-13} [H^+]^{-2.16} p_{SO_2} \quad (25^\circ C, p_{SO_2} \text{ in atm}) \end{aligned}$$

Or, expressed in terms of $[HSO_3^-]$:

$$\begin{aligned} v &= 1.2 \times 10^{-4} K_2 [H^+]^{-1.16} [HSO_3^-] \approx \\ &\approx 7.4 \times 10^{-12} [H^+]^{-1.16} [S(IV)] \quad (25^\circ C) \end{aligned}$$

K_1, K_2, H are the first and second dissociation constants and the Henry coefficient.

Penkett et al. (1979) obtain

$$v = k[S(IV)] \quad \text{with } k = 2.74 \times 10^{-6} \text{ over the range } 4 < \text{pH} < 7.$$

Larson et al. (1978) find the following expression:

$$v = \{4.8 \times 10^{-3} + 8.9 [H^+]^{\frac{1}{2}} + 3.9 \times 10^{-12} p_{O_2} [H^+]^{-1}\} [SO_3^{2-}]$$

$$\approx \{4.8 \times 10^{-3} + 8.9 [H^+]^{\frac{1}{2}} + 3.9 \times 10^{-12} p_{O_2} [H^+]^{-1}\} \frac{K_2}{[H^+]} [S(IV)]$$

Example:

As an example, we take

$$[S(IV)] = 10^{-5}$$

$$[H^+] = 10^{-5}$$

(p_{O_2} is immaterial, because the corresponding term is negligible)

$$\begin{aligned} \text{Beilke et al.'s equation gives: } v &= 4.7 \times 10^{-11} \text{ M s}^{-1} \\ &= 2.8 \times 10^{-9} \text{ M min}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Penkett et al.'s equation gives: } v &= 2.7 \times 10^{-11} \text{ M s}^{-1} \\ &= 1.6 \times 10^{-9} \text{ M min}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Larson et al.'s equation gives: } v &= 2 \times 10^{-9} \text{ M s}^{-1} \\ &= 1.2 \times 10^{-7} \text{ M min}^{-1} \end{aligned}$$

The discrepancy of the last result is large, but all rates are too small to be of major importance (even the last rate only represents 1.2% oxidation per minute).

4. Catalyzed oxidation

The oxidation of SO_2 by O_2 is catalyzed by transition metals of the 4th period of the table of elements, especially Mn and Fe. The effects of catalysts was investigated by a number of authors (Barrie and Georgii, 1976; Coughanowr and Krause, 1965; Bracewell and Gall, 1967; Tsunogai, 1971; Brimblecombe and Spedding, 1974; Betz, 1977; Beilke and Gravenhurst, 1978; Fuzzi, 1978). Beilke and Gravenhurst comment on previous work, and we shall here mention particularly his conclusions and some other results by Fuzzi.

Fuzzi found that in the case of Fe(III) in solution, the oxidation proceeds according to

$$v = k[\text{S(IV)}]^n [\text{Fe(III)}]$$

where $n = 1$ for pH: 3-4

$n = 2$ for pH: 5

$n = \text{intermediate}$, in the range pH: 4-5; in this range, Fe^{3+} becomes precipitated as Fe(OH)_3 and is all in that form for pH > 5.

Illustrative values for $[\text{S(IV)}] = 10^{-4}\text{M}$, $[\text{Fe(III)}] = 2 \times 10^{-6}\text{M}$ are:

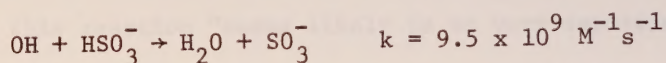
pH	$v \text{ (M s}^{-1}\text{)}$
3	6×10^{-4}
4	32.6×10^{-4}
5	2.3×10^{-4}
6	1.3×10^{-4}

These are very high rates, but other than the high $[S(IV)]$ assumed, the concentration assumed of $Fe(III)$ can only be expected in highly polluted air (clouds and fogs formed by urban air or air polluted by industries). For instance, a cloud condensation nucleus of 10^{-15} g with 10% of $Fe(III)$ would give a drop of 10 μ m radius with $[Fe(III)] \sim 5 \times 10^{-7} M$ (cf. calculation of aerosol produced alkalinity, in Section I.3). Beilke and Gravenhurst come to the same conclusion regarding the experiments of Barrie and Georgii (1976), noting that in urban air clouds and fogs, the catalysts concentrations (Mn, Fe) can be of the order of $10^{-5} M$ or even higher.

The comparison of results of the various authors with those for non-catalyzed oxidation by O_2 shows that the sulfate formation may proceed about two or three orders of magnitude faster when the catalysts are present.

5. Oxidation by OH and HO_2

The radical OH reacts with HSO_3^- according to



followed by further reactions of SO_3^- with final production of $SO_4^{=}$ (CD).

It might provide in principle another oxidation path, with a reaction velocity

$$v = k [OH] [HSO_3^-]$$

For instance, with $[HSO_3^-] \approx [S(IV)] = 10^{-5} M$ and taking the concentration of OH calculated by CD as $3.5 \times 10^{-13} M$ (dependent on drop size distribution and cloud transmissivity), one obtains

$$v = 3 \times 10^{-8} M s^{-1} = 1.8 \times 10^{-6} M \text{ min}^{-1}$$

This is a high value, and CD speculate that oxidation by OH "may represent a significant and in some cases a primary pathway by which dissolved S in the +4 oxidation state is converted to $\text{SO}_4^=$ " (p. 4875; Table 7). However, this is not so. CD base their argument on the previous rates of reaction and the lifetimes calculated as

$$\tau = 1/k [\text{OH}]$$

($\tau = 250$ s for similar conditions to those used above). This is misleading, because $[\text{OH}]$ is far from constant; in fact it is $\ll [\text{HSO}_3^-]$ and OH will become immediately depleted. The production of OH in the liquid will then become the rate-determining process. The total production rate, according to their Table 5, is about $10^{-9} \text{ M s}^{-1} = 6 \times 10^{-8} \text{ M min}^{-1}$, and this is a negligible rate for the production of sulfate.*

GW mention the oxidation of S(IV) by direct reaction with HO_2 :



and express that this reaction "seems likely to be very important in aqueous aerosols, since it provides an efficient path for the conversion of SO_2 to $\text{SO}_4^=$ and at the same time regenerates the reactive hydroxyl radical from the less reactive HO_2 ." However, the same objection may be made here as for OH: $[\text{HO}_2]$ is only 10^{-9} to 10^{-8} M in the liquid (CD, Table 5) and can only be replaced at a production rate of 10^{-9} to 10^{-8} M s^{-1} , or approximately 10^{-7} to $10^{-6} \text{ M min}^{-1}$. Only in marginal conditions (high cloud transmissivity, droplet spectrum predominantly in the small size range) could

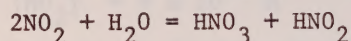
* The argument of CD may be valid for their cloud model for remote areas, with a very low SO_2 concentration (55 ppt(v) in the air).

this be significant.

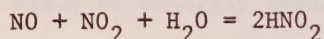
The radical HO_2 , on the other hand, may be more important through its role in the production of H_2O_2 . This has been discussed in the section devoted to this oxidant.

6. Oxidation by oxo compounds of nitrogen

Martin et al. (1981) have studied experimentally the oxidation of SO_2 by NO_3^- , NO_2^- and NO . The results are also interesting in principle regarding NO_2 , linked to the previous species by the disproportionation reaction in aqueous solution:



and by the gaseous reaction



However, their results indicate that the possible oxidation paths are not important. Oxidation by NO_3^- and NO were shown to be entirely negligible.

As for NO_2^- - a stronger oxidant - the reaction is faster, giving N_2O and $\text{SO}_4^{=}$ as products. The kinetic equation is

$$v = k [\text{H}^+]^{\frac{1}{2}} [\text{N(III)}] [\text{S(IV)}]$$

where $[\text{N(III)}] = [\text{HNO}_2] + [\text{NO}_2^-]$. The value of the rate constant is

$$k = 142 \text{ M}^{-3/2} \text{ s}^{-1}$$

and the reaction is not catalyzed by Fe^{3+} , Mn^{2+} or VO^{2+} .

The gaseous concentration of HNO_2 may be only a few ppb(v) in polluted urban air (Martin et al., 1981; Leighton, 1961, p.191). This leads to negligible oxidation rates, even for polluted air.

Example:

$$[\text{H}^+] = 10^{-5}, [\text{S(IV)}] = 10^{-5}$$

Concentration of HNO_2 in air: 3 ppb(v) (3×10^{-9} atm, at 1 atm)

Henry's coefficient for HNO_2 : $H = 47.6 \text{ M atm}^{-1}$ (25°C)

Dissociation constant : $K = 5.9 \times 10^{-4}$ (25°C)

From these constants, it may be derived that

$$[\text{HNO}_2] = 1.5 \times 10^{-7} \text{ M}$$

$$[\text{NO}_2^-] = 9 \times 10^{-6} \text{ M}$$

Therefore $[\text{N(III)}] \approx 9 \times 10^{-6} \text{ M}$

$$\text{and } v = 4 \times 10^{-11} \text{ M s}^{-1} = 2.4 \times 10^{-9} \text{ M min}^{-1}$$

which is entirely negligible.

The more abundant nitrous oxide N_2O is an inert gas and needs not be considered.

7. Conclusions on SO_2 oxidation in cloud water: Two numerical examples

From the previous review it appears that only H_2O_2 , O_3 and HO_2 are oxidants capable of producing appreciable oxidation during the life time of cloud droplets. To this, the possibility of fast catalyzed oxidation should be added, if efficient metal catalysts are present in the atmospheric aerosol.

According to the conditions of the cloud system (concentration of SO_2

and NH_3 , alkalinity of aerosol; see Chapter on equilibrium conditions), the fraction of SO_2 that becomes dissolved in the cloud water will vary. Two extreme cases can be considered: 1) most SO_2 becomes dissolved and 2) the fraction dissolved is $\ll 1$. In the first case, SO_2 cannot be replaced in the liquid phase as it becomes depleted by oxidation; in the latter case, it can be assumed that dissolution is fast enough to maintain a constant $[\text{S(IV)}]$. For these two extreme cases, integrations can be performed, to indicate the amount of sulfate production as a function of time. This has been done in Appendices E and F.

As Fig. 1 shows the resulting curve from the integration for the first case is very well represented by

$$[\text{S(VI)}] = 10^{-5}(1 - e^{-t/\tau}), \text{ with } \tau = 2.0 \text{ min}$$

for the conditions of the example of Appendix E (with initial $[\text{S(IV)}] = 10^{-5}\text{M}$). If in a parameterization one would like to separate the two oxidations, the percentage due to each oxidant can be estimated as shown in the figure.

The results for the second case, with the parameters chosen for the example, are shown in Fig. 2.

8. The effect of SO_2 oxidation in liquid phase on acidity

The two previous examples, although illustrating extreme cases of solubilization, are oversimplified in that they ignore the influence of the oxidation on the pH, and therefore on the fraction dissolved. This problem will now be examined.

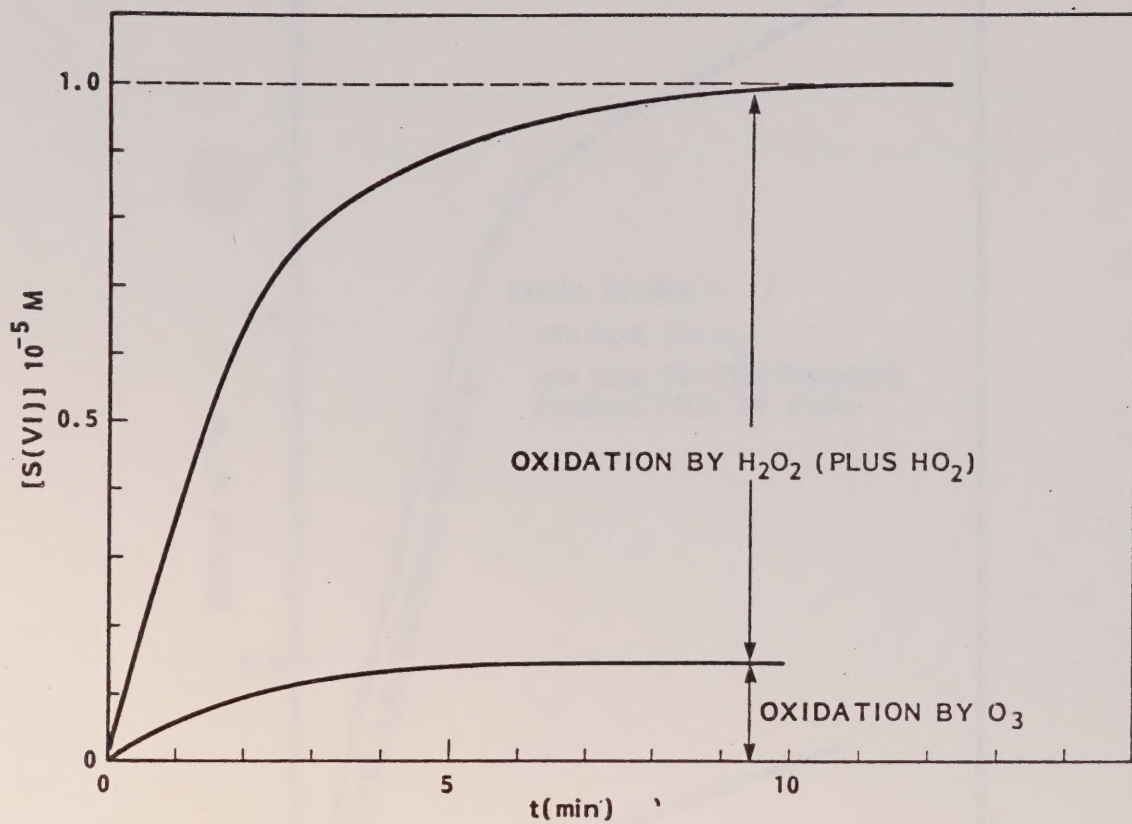


Fig. II.1

PRODUCTION OF SO_2^- ($[\text{S(VI)}]$) WITH LIMITED
INITIAL CONCENTRATION OF SO_2 IN SOLUTION

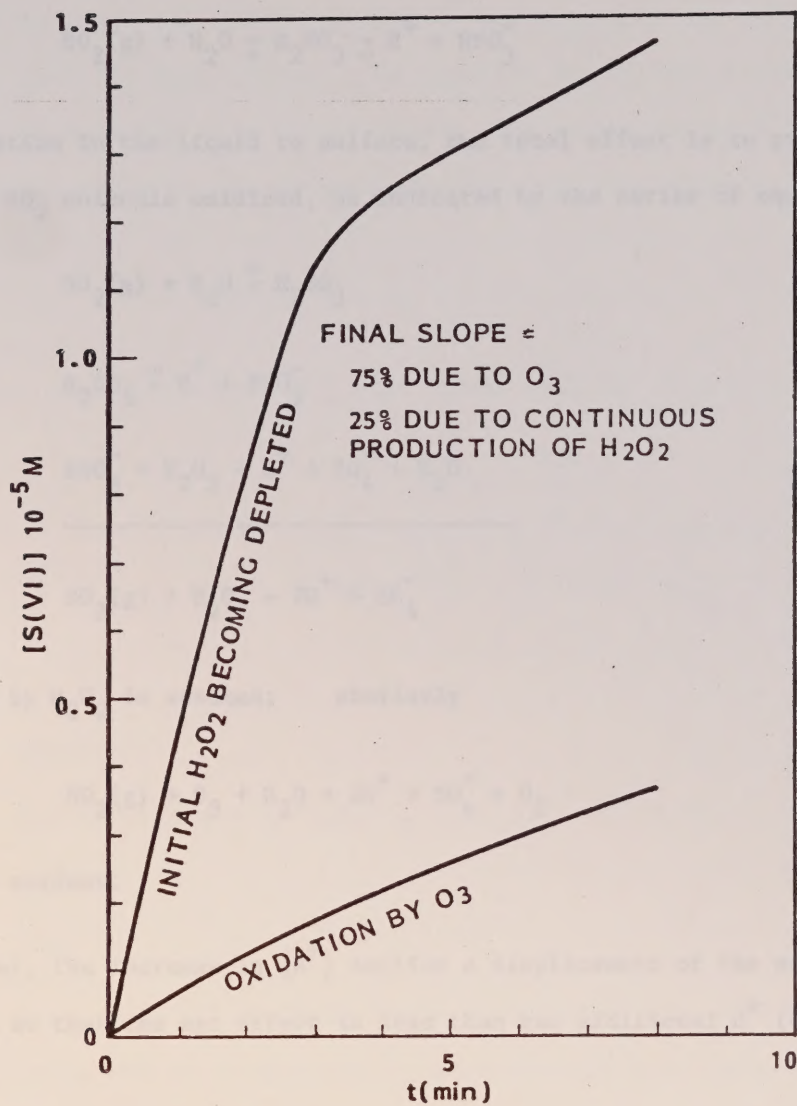
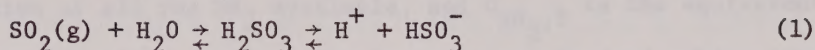


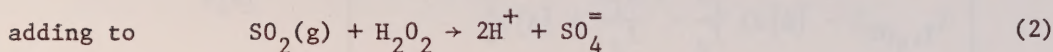
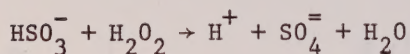
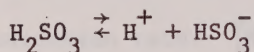
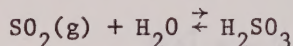
Fig. II.2

PRODUCTION OF SO_4^{2-} $[\text{S(VI)}]$
 WITH CONTINUAL REPLENISHMENT OF
 SO_2 IN SOLUTION

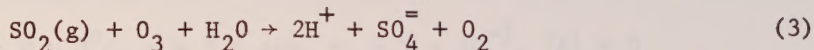
When considering the chain of equilibria



and the oxidation in the liquid to sulfate, the total effect is to produce 2H^+ for each SO_2 molecule oxidized, as indicated by the series of equations



if oxidation by H_2O_2 is assumed; similarly



if O_3 is the oxidant.

However, the increase in $[\text{H}^+]$ implies a displacement of the equilibria to the left, so that the net effect is less than two additional H^+ (cf. Ch. I, Section 11).

The calculation can be done with sufficient approximation by the simplified treatment discussed in Chapter I, Section 10. It was there seen that $[\text{H}^+]$ could be calculated (eq. (26)) from:

$$[\text{H}^+] = -\frac{1}{2} \left([\text{A}] + \frac{kK_1}{k} \right) + \sqrt{\frac{1}{4} \left([\text{A}] + \frac{kK_1}{k} \right)^2 - \frac{K_1}{k} (k[\text{A}] - c_{\text{SO}_2, \text{T}})} \quad (4)$$

Here $[A]$ represents the alkalinity term provided by the CCN and by the initial dissolution of all the NH_3 available, and $C_{\text{SO}_2, T}$ is the equivalent total mixing ratio for both phases. The equation was derived taking into account mass conservation in a closed system. The production of H^+ by SO_2 oxidation during a time δt can be considered as a negative addition to the parameter $[A]$:

$$\delta[A] = -2 v \delta t \quad (5)$$

where v is the oxidation rate. $[\text{H}^+]$ will change with $[A]$ according to

$$\frac{\partial [\text{H}^+]}{\partial [A]} = \frac{1}{2} \left[-1 + \frac{\frac{1}{2} \left([A] - \frac{K_1 k}{k_1} \right)}{\frac{1}{4} \left([A] + \frac{K_1 k}{k_1} - \frac{K_1}{k_1} (k[A] - C_{\text{SO}_2, T}) \right)} \right] \quad (6)$$

Example:

For $T = 0^\circ\text{C}$, $p = 0.6 \text{ atm}$, $r_L = 5 \times 10^{-3}$, $[A] = 0$

$$\frac{\partial [\text{H}^+]}{\partial [A]} = -0.54$$

I.e., only 54% of the H^+ produced increases the acidity; the other 46% has disappeared by causing a shift in the solubility equilibrium.

The increase in $[\text{H}^+]$ due to oxidation will also have an effect on the oxidation rate itself, according to the kinetics of oxidation by H_2O_2 and O_3 .

Therefore, the effects of the SO_2 oxidation will be:

- 1) An increase in acidity, as given in formula (6). This will be accompanied by a shifting of the equilibria, and therefore by a decrease in the

fraction of SO_2 dissolved.

- 2) The rate of oxidation by H_2O_2 , which is $\propto [\text{HSO}_3^-][\text{H}^+]$ will be modified accordingly. Here $[\text{HSO}_3^-]$ decreases (consumption and equilibrium shifting) and $[\text{H}^+]$ increases.
- 3) The rate of oxidation by O_3 will decrease, as it can be written $\propto [\text{HSO}_3^-][\text{H}^+]^{-0,4}$ or $\propto [\text{HSO}_3^-][\text{H}^+]^{-0,85}$ (representing Maahs's results (1983))(cf. section 2).

9. Oxidation of SO_2 by O_3 in a cloud. A numerical example taking into account the equilibrium between liquid and gaseous phases.

As seen in the previous section, the production of acidity during oxidation alters the SO_2 solubility. It also alters the reaction rates according to the values of HSO_3^- , H^+ , and O_3 or H_2O_2 . It is therefore desirable to develop a numerical example more realistic than those of section 7, that will give an idea of the times required for the SO_2 oxidation and how they compare with the life time of liquid water in clouds. This has been done for O_3 oxidation only, in order to simplify the calculation.

The details of this numerical estimate are given in Appendix G. Rather drastic simplifications were introduced. The total concentration of SO_2 was taken as 10 ppb(v) and two examples were considered: 1) cloud water is pure, 2) cloud water has an initial $\text{pH} = 4.0$.

The results of the computations are summarized in Fig. 3 for both examples. For each example, $c_T(V)$ and pH are given as functions of time, up to 30 hours.

A number of points can be made on the basis of these results:

1. The initial pH of the cloud water has an important influence. The concentration of dissolved SO_2 is inversely proportional to $[H^+]$ and directly proportional to the remaining $c(V)$ in the air (cf. eq. (2) in Appendix G). The latter increases with $[H^+]$, but less than proportionally (cf. eq. (6)). Thus for lower pH, less SO_2 is dissolved and the reaction rate becomes smaller (cf. eq. (1)). This is clearly reflected in the difference between the curves for Examples 1 and 2.

Thus the rate of oxidation will depend appreciably on the initial pH of cloud water, and this depends on

- (a) Aerosol characteristics. Droplets of H_2SO_4 already present, particles of NH_4HSO_4 or even $(NH_4)_2SO_4$, NH_4Cl or NH_4NO_3 will tend to lower the pH. $CaCO_3$ will tend to raise it.
- (b) Presence of NH_3 or HNO_3 in the gas phase. The former will contribute to alkalinity, and its influence was already discussed in the chapter on equilibrium. The latter will lower the pH.

2. The presence and subsequent oxidation of SO_2 also influence the pH. The oxidation produces H^+ ions, thus producing a negative self-catalysis of the reaction. This is reflected in the decrease of the negative slope of the curves $c_T(V) = f(t)$ in Fig. 3.

This negative self-catalysis is quite pronounced if the initial pH is high (Example 1: initial pH of 4.68 being reduced to 4.0 in 3 hours), but much less important when the pH is lower (Example 1, after 3 h and Example 2, from the beginning). The reduction of pH, for a given amount

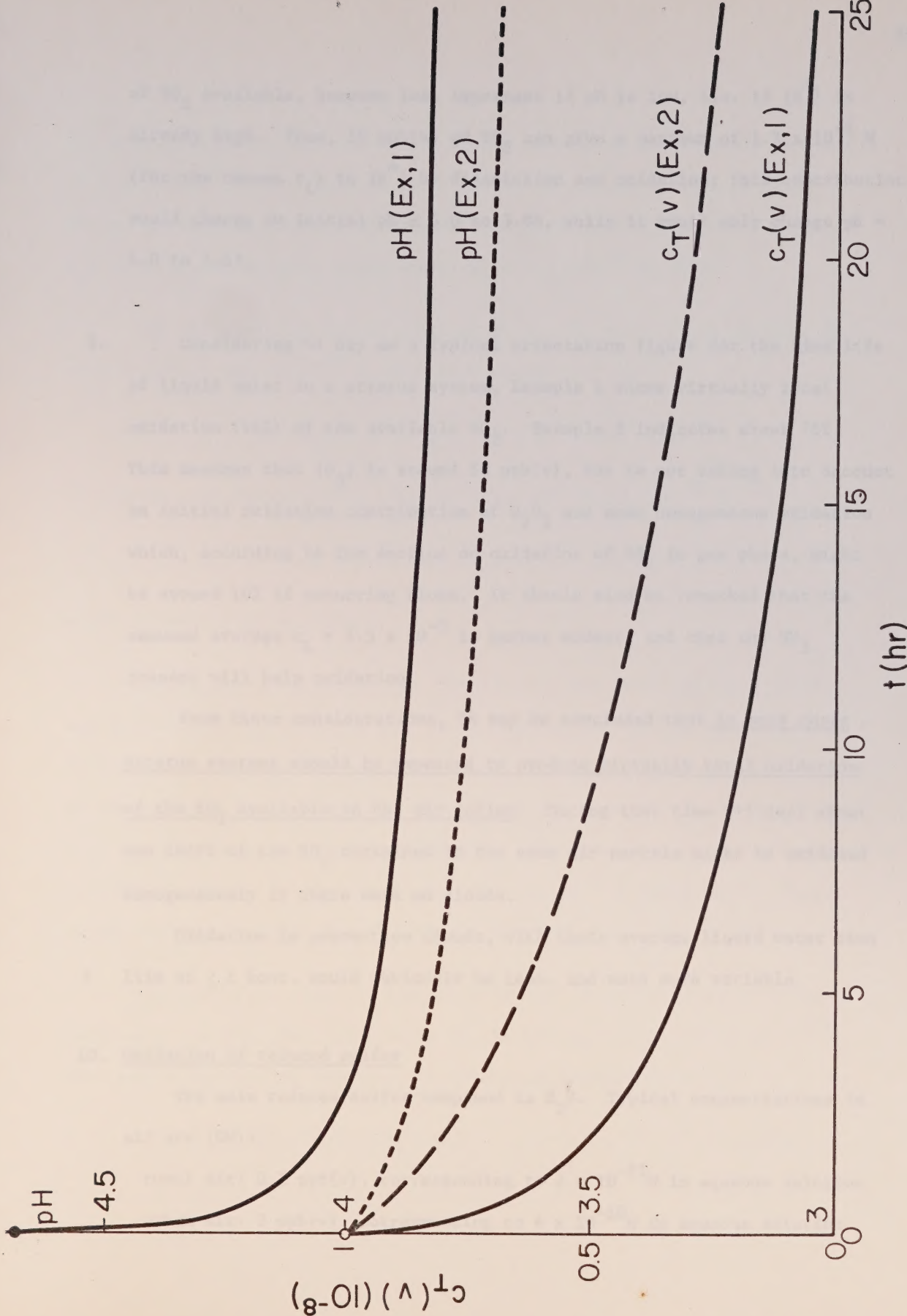


Fig. II.3 - Production of SO_4^{2-} by O_3 oxidation and variation of pH, taking into account the variation of fraction of dissolved SO_3 , for two examples (see text).

of SO_2 available, becomes less important if pH is low, i.e. if $[\text{H}^+]$ is already high. Thus, 10 ppb(v) of SO_2 can give a maximum of 1.3×10^{-4} M (for the chosen r_L) to $[\text{H}^+]$ by dissolution and oxidation; this contribution would change an initial pH = 6.0 to 3.88, while it would only change pH = 4.0 to 3.63.

3. Considering ~ 1 day as a typical orientation figure for the time life of liquid water in a stratus system, Example 1 shows virtually total oxidation (94%) of the available SO_2 . Example 2 indicates about 75%. This assumes that $[\text{O}_3]$ is around 50 ppb(v), but is not taking into account an initial oxidation contribution of H_2O_2 and some homogeneous oxidation which, according to the section on oxidation of SO_2 in gas phase, might be around 10% if occurring alone. It should also be remarked that the assumed average $r_L = 2.5 \times 10^{-3}$ is rather modest, and that any NH_3 present will help oxidation.

From these considerations, it may be concluded that in most cases, stratus systems should be expected to produce virtually total oxidation of the SO_2 available in the air influx. During that time (~ 1 day) about one third of the SO_2 contained in the same air parcels might be oxidized homogeneously if there were no clouds.

1. Oxidation in convective clouds, with their average liquid water time life of ≤ 1 hour, would obviously be less, and much more variable.

10. Oxidation of reduced sulfur

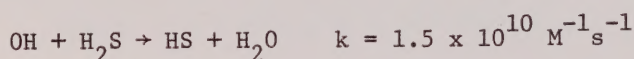
The main reduced sulfur compound is H_2S . Typical concentrations in air are (GW):

rural air: 0.1 ppb(v), corresponding to 2×10^{-11} M in aqueous solution

urban air: 2 ppb(v), corresponding to 4×10^{-10} M in aqueous solution

The concentrations in the liquid correspond to a value of the Henry constant of 0.20 M Atm^{-1} (0°C). These will be the values in cloud water, because due to the small solubility the gaseous concentration will remain constant. H_2S is only very slightly dissociated ($K_1 = 5.7 \times 10^{-8}$ at 25°C).

The dissolved H_2S may be oxidized by O_2 , OH , etc. If we consider OH , with a typical $[\text{OH}] \approx 10^{-12} \text{ M}$, and the reaction



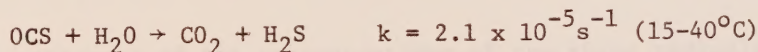
as a first step for oxidation (GW), we have, for $[\text{H}_2\text{S}] = 10^{-10} \text{ M}$:

$$v = 1.5 \times 10^{10} \times 10^{-12} \times 10^{-10} = 1.5 \times 10^{-12} \text{ M s}^{-1}$$

which is completely negligible.

H_2S is also oxidized by O_2 . The kinetic data from various authors are inconsistent and indicate half lives (uncatalyzed oxidation) from 24 to 10,000 min for similar concentration ranges (Hoffmann and Lim, 1979). Catalysis by impurities might increase the rates. However, even if all the H_2S coming into the cloud were dissolved and oxidized, this would amount to a concentration of products (S(IV)) in the cloud water of $1.4 \times 10^{-6} \text{ M}$ (rural air). Thus, except for very polluted air, H_2S can be ignored as a source of S(IV) .

OCS can be in a typical concentration of 0.6 ppb(v) (both rural and urban air; see GW), corresponding to an equilibrium concentration of 10^{-11} M . This gas is hydrolyzed, providing an additional production of H_2S :



This first-order constant corresponds to a half life of 9.2 hours. The velocity is given by

$$v = 2.1 \times 10^{-5} \times 10^{-11} = 2.1 \times 10^{-16} \text{ M s}^{-1}.$$

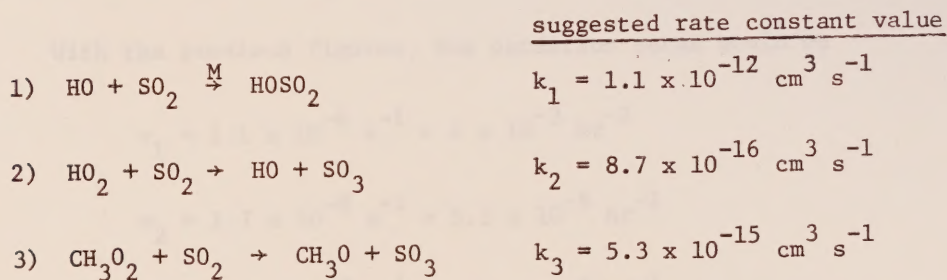
This is clearly insignificant.

CS₂ exists in even smaller concentrations than H₂S and OCS, and need not be considered.

C. OXIDATION OF SO₂ IN GAS PHASE

This is of course a subject that has been treated by many researchers along a number of years.

A summary of the various paths for homogeneous oxidation of SO₂ in the troposphere according to modern information has been made by Calvert et al. (1978). These authors conclude that in the natural (nonpolluted) troposphere, the oxidation occurs largely by way of the following reactions, the first one being the dominant path:



With appropriate estimates of the concentrations of the three radicals, the total rate of SO₂ oxidation is estimated at 1.5% hr⁻¹ at midday in July in midlatitudes.

In a cloud, the conditions are different. A cloud transmissivity smaller than unity (say, between 0.1 and 0.5) for the solar radiation must be taken into account, and the radicals are being scavenged by the cloud droplets. Chameides and David (1982) have studied this situation, and suggest the following concentration values, for a zenith angle of 30° :

$$[\text{OH}] : 3 \times 10^5 \text{ to } 3 \times 10^6 \text{ cm}^{-3}$$

$$[\text{OH}_2] : 2 \times 10^6 \text{ to } 2 \times 10^8 \text{ cm}^{-3}$$

where the values are not only dependent on the cloud transmissivity, but also on the badly known accommodation or sticking coefficient. As orientation figures, the estimates

$$[\text{OH}] \sim 10^6 \text{ cm}^{-3}$$

$$[\text{HO}_2] \sim 2 \times 10^7 \text{ cm}^{-3}$$

seem appropriate (see l.c., Fig. 3, p.4868). For CH_3O_2 , an orientation figure could be $[\text{CH}_3\text{O}_2] \sim 10^7 \text{ cm}^{-3}$ (cf. Calvert et al., p.209). Higher figures should be expected in highly polluted atmospheres.

With the previous figures, the oxidation rates would be

$$v_1 = 1.1 \times 10^{-6} \text{ s}^{-1} = 4 \times 10^{-3} \text{ hr}^{-1}$$

$$v_2 = 1.7 \times 10^{-8} \text{ s}^{-1} = 5.3 \times 10^{-5} \text{ hr}^{-1}$$

$$v_3 = 5.3 \times 10^{-8} \text{ s}^{-1} = 1.9 \times 10^{-4} \text{ hr}^{-1}$$

and the total rate of oxidation can be estimated as

$$v = - \frac{d[\text{SO}_2]}{dt} \sim 4.2 \times 10^{-3} [\text{SO}_2]$$

or

$$- \frac{d \ln[\text{SO}_2]}{dt} \sim 4.2 \times 10^{-3} \text{ hr}^{-1} = 1.2 \times 10^{-6} \text{ s}^{-1}$$

i.e., $0.42\% \text{ hr}^{-1}$ or about one third of the value for the conditions indicated by Calvert et al.

According to this estimate, gas phase oxidation of SO_2 can be neglected in a convective cloud, where the air parcels remain typically less than one hour. For stratiform clouds, where the permanency may reach up to the order of 100 hr, gas phase oxidation may become quite important.

It must be considered that the effect of the clouds is being studied in reference to the normal rates of reaction in clear air as a background situation. That is, the effect of a cloud is to reduce the rate of gas-phase oxidation to about one third of what would happen without the cloud, and superimpose to it the rate of oxidation in cloud water (which will be considerably higher).

D. IN-CLOUD CHEMISTRY OF N COMPOUNDS

The chemistry of N compounds involves the following species:

N (II) : NO nitrogen oxide

N (III): N_2O_3 dinitrogen trioxide or nitrous anhydride

HNO_2 nitrous acid

N (IV) : NO_2 nitrogen dioxide

N (V) : N_2O_5 dinitrogen pentoxide or nitric anhydride

HNO_3 nitric acid

Also involved are: NO_3 , reactive radical produced in gas phase by oxidation of NO_2 by O_3 , and the peroxyntitric acid HO_2NO_2 . The more abundant nitrous oxide N_2O is very inert and not considered a pollutant; therefore it will not be included in the present study.

The primary purpose in this summary is to consider the possible pathways leading from NO_x (i.e. NO or NO_2) in the gaseous phase to nitric acid in cloud water. From the numerous reactions of the nitrogen compounds, only those relevant to that purpose will be taken into consideration.

Solubilities of N oxo compounds

This subject has been thoroughly examined by Schwartz and White (1981).

1. NO

The solubility in water is slight. Values of Henry's coefficient are

$$H = 3.3 \times 10^{-3} \text{ M atm}^{-1} \text{ at } 0^{\circ}\text{C}$$

$$H = 1.9 \times 10^{-3} \text{ M atm}^{-1} \text{ at } 25^{\circ}\text{C}$$

This indicates that the NO absorbed by cloud water must be entirely negligible, unless it participates in a chemical reaction.

Example:

$$p_{\text{NO}} = 10^{-9} \text{ atm}$$

At 0°C , the equilibrium concentration is $[\text{NO}] = 3.3 \times 10^{-12} \text{ M}$

For a cloud with $r_L = 5 \times 10^{-3}$, only a fraction 5×10^{-7} of the NO would be in the liquid phase.

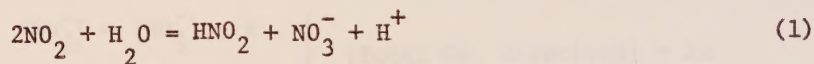
2. NO_2

Henry's coefficient is

$$H = 7.0 \times 10^{-3} \text{ M atm}^{-1} \quad (22^{\circ}\text{C})$$

(Lee and Schwartz, 1981).

Dissolution in water is followed by the reaction



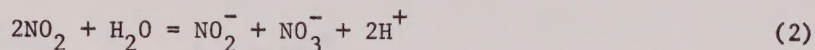
with the overall equilibrium constant

$$K = \frac{[\text{HNO}_2][\text{NO}_3^-][\text{H}^+]}{p_{\text{NO}_2}^2} = 4.3 \times 10^5 \text{ M}^3 \text{ atm}^{-2}$$

(Pick, 1920). Although HNO_2 is a weak acid, with a dissociation constant

$$K_1 = \frac{[\text{NO}_2^-][\text{H}^+]}{[\text{HNO}_2]} = 5.1 \times 10^{-4}$$

if the solution is very diluted, the acid may be mostly dissociated. In that case, instead of (1) the total reaction would be



and the overall constant would be

$$KK_1 = \frac{[\text{NO}_2^-][\text{NO}_3^-][\text{H}^+]^2}{P_{\text{NO}_2}^2} = 2.2 \times 10^2 \text{ M}^4 \text{ atm}^{-2} \quad (3)$$

If NO_2 is in the ppb range, it should be expected that, in equilibrium, most of the NO_2 would be in the aqueous phase (as the products of the reaction) and the HNO_2 would be mostly dissociated.

Example:

Air flowing into a cloud contains 2.5 ppb(v) of NO_2 :
 $C_T(v) = 2.5 \times 10^{-9}$ (assuming that pressure $p = 1 \text{ atm}$, for simplicity). According to (2) (and assuming that the cloud consists of pure water droplets)

$$\left. \begin{array}{l} [\text{NO}_2^-] = [\text{NO}_3^-] = x \\ [\text{H}^+] = 2x \end{array} \right| \quad [\text{Total NO}_2 \text{ dissolved}] = 2x$$

$$\left\{ \begin{array}{ll} 10^{-3} \rho_w^{-1} \mu_a r_L (2x) + C_T(v) = C_T(v) & \text{Conservation of NO}_2 \\ 4x^4 = 2.2 \times 10^2 \times [C_T(v) \cdot p]^2 & \text{Equation (3)} \end{array} \right.$$

that

Solving the equations with $r_L = 5 \times 10^{-3}$, it is found that

$$x = 8.6 \times 10^{-6} \text{ M, pH} = 4.8$$

$$C(v) = 10^{-11}$$

$$\frac{C(v)}{C_T} = 3.4 \times 10^{-8} \text{ (fraction remaining in gas phase)}$$

HNO_2 is almost completely dissociated, because

$$\frac{[\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{K_1}{[\text{H}^+]} = \frac{5.1 \times 10^{-4}}{1.7 \times 10^{-5}} = 30$$

It will be seen, however, that equilibrium is not reached by far, in the time available in a cloud.

3. HNO_2

The solubility is high, with a Henry coefficient

$$H = 49 \text{ M atm}^{-1} \quad (25^\circ\text{C})$$

(Schwartz and White, 1981).

A pseudo Henry's law coefficient H^* can be defined, for convenience, as the total concentration of dissolved species (i.e., $[\text{HNO}_2] + [\text{NO}_2^-]$ in this case), in molarity, over the partial pressure of the gas (p_{HNO_2}), in atmospheres (see for instance: Ogram, 1982). This varies for HNO_2 , from 74 at $\text{pH} = 3$, to 2.5×10^4 at $\text{pH} = 6$.

To obtain the fraction of HNO_2 that will dissolve in equilibrium, the following equations can be written:

$$\begin{cases} 10^{-3} \rho_w^{-1} \mu_a r_L [\text{Total HNO}_2 \text{ dissolved}] + C_T(v) = C_T(v) \\ [\text{Total HNO}_2 \text{ dissolved}] = H^* C_T(v) p \end{cases}$$

From where the fraction dissolved is seen to be

$$\frac{10^{-3} \rho_w^{-1} \mu_a r_L H^* p}{10^{-3} \rho_w^{-1} \mu_a r_L H^* p + 1}$$

which, for $p = 1 \text{ atm}$, $r_L = 5 \times 10^{-3}$, goes from 1% at $\text{pH} = 3$ to 78% at $\text{pH} = 6$.

4. HNO₃

The solubility is extremely high:

$$H = 2.1 \times 10^5 \text{ M atm}^{-1} \quad (25^\circ\text{C})$$

$$H^* = 3.2 \times 10^9 \quad \text{at pH} = 3$$

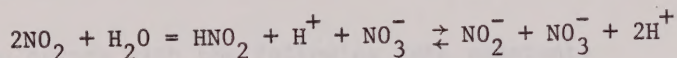
$$3.2 \times 10^{12} \quad \text{at pH} = 6$$

Performing the same computation as above, it becomes clear that practically all HNO₃ will dissolve in the cloud water, at equilibrium.

E. REACTIONS OF NITROGEN COMPOUNDS IN LIQUID PHASE

1. Disproportionation reaction of dissolved NO₂

This is the reaction described in the section on solubility of NO₂:



At first sight, it is an obvious possible pathway for the production of HNO₃. However, the reaction was kinetically studied by Lee and Schwartz (1981), who derived the Henry coefficient already mentioned and the rate constant given below:

$$v = k [\text{NO}_2]^2, \quad k = 1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \quad (22^\circ\text{C})$$

$$= k H^2 p_{\text{NO}_2}^2$$

This value indicates that no significant production of HNO₃ can occur in the time available to cloud droplets.

Example:

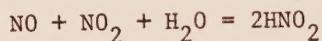
$$p_{\text{NO}_2} = 2.5 \times 10^{-9} \text{ atm}$$

$$v = 1.0 \times 10^8 \times (7.0 \times 10^{-3})^2 \times (2.5 \times 10^{-9})^2$$

$$= 3 \times 10^{-14} \text{ M s}^{-1} = 1.1 \times 10^{-10} \text{ M hr}^{-1}$$

2. Production of HNO₂ from NO and NO₂

Dissolved NO and NO₂ may react according to



2. THEORY OF THE LINEAR TRANSFORMATION

2.1. DEFINITION OF THE LINEAR TRANSFORMATION

This is the linear transformation in the vector space V over F .

$$T(a_1x_1 + a_2x_2 + \dots + a_nx_n) = a_1T(x_1) + a_2T(x_2) + \dots + a_nT(x_n)$$

At this stage, it is an abstract vector space and the definition of T . However, the linear transformation T is defined by the matrix A and the vectors $x_1, x_2, \dots, x_n$ are defined by the matrix X and the vectors $T(x_1), T(x_2), \dots, T(x_n)$ are defined by the matrix Y .

Thus we have

$$Y = AX$$

$$Y = AX$$

This is the linear transformation T in the vector space V over F .

The matrix A is called the matrix of T .

Example:

$$T(x_1) = x_1 + x_2$$

$$T(x_2) = x_1 - x_2$$

$$T(x_3) = x_1 + x_2 + x_3$$

2.2. THEORY OF THE LINEAR TRANSFORMATION

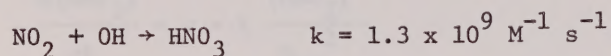
Definition: A linear transformation T is called a linear transformation if

$$T(a_1x_1 + a_2x_2 + \dots + a_nx_n) = a_1T(x_1) + a_2T(x_2) + \dots + a_nT(x_n)$$

The importance of this reaction is not well established, but in view of the low solubility of NO it seems unlikely that it be significant in clouds. (cf. GW; Schwartz and White, 1981, equilibrium M2).

3. Oxidation of NO₂ by OH

This reaction occurs with the following rate constant:



$$v = k [\text{NO}_2] [\text{OH}]$$

(see CD).

This velocity is negligible.

Example:

$$p_{\text{NO}_2} = 10^{-8} \text{ atm (10 ppb at 1 atm)}$$

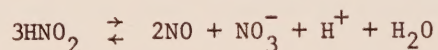
$$[\text{NO}_2] = K_{\text{H}} p_{\text{NO}_2} = 7 \times 10^{-3} \times 10^{-8} = 7 \times 10^{-11} \text{ M}$$

$$[\text{OH}] = 3.5 \times 10^{-13} \text{ (as typical value; see CD)}$$

$$v = 3 \times 10^{-14} \text{ M s}^{-1} = 1.1 \times 10^{-10} \text{ M hr}^{-1}$$

4. Disproportionation reaction of HNO₂

HNO₂ is known to decompose in solution, according to



The reaction is reversible, with an equilibrium constant

The following is a list of the most important results of the theory of the stability of the equilibrium of a system of particles. The results are given in the form of theorems and lemmas. The first theorem is the most important one. It states that if the potential energy of a system of particles is a function of the coordinates only, then the system is stable if and only if the potential energy is a minimum at the equilibrium position.

3. Theorem of the stability of the equilibrium of a system of particles.

This theorem states that the following conditions are necessary and sufficient for the stability of the equilibrium of a system of particles:

$$V(x_1, x_2, \dots, x_n) = V(x_1^0, x_2^0, \dots, x_n^0) + \frac{1}{2} \sum_{i,j=1}^n \frac{\partial^2 V}{\partial x_i \partial x_j} (x_1^0, x_2^0, \dots, x_n^0) (x_i - x_i^0) (x_j - x_j^0) + \dots$$

$$V(x_1^0, x_2^0, \dots, x_n^0) = V(x_1^0, x_2^0, \dots, x_n^0)$$

where V is the potential energy of the system.

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$$V(x_1^0, x_2^0, \dots, x_n^0) = V(x_1^0, x_2^0, \dots, x_n^0)$$

$$V(x_1^0, x_2^0, \dots, x_n^0) = V(x_1^0, x_2^0, \dots, x_n^0)$$

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$$V(x_1, x_2, \dots, x_n) = V(x_1^0, x_2^0, \dots, x_n^0) + \frac{1}{2} \sum_{i,j=1}^n \frac{\partial^2 V}{\partial x_i \partial x_j} (x_1^0, x_2^0, \dots, x_n^0) (x_i - x_i^0) (x_j - x_j^0) + \dots$$

The following is a list of the most important results of the theory of the stability of the equilibrium of a system of particles. The results are given in the form of theorems and lemmas. The first theorem is the most important one. It states that if the potential energy of a system of particles is a function of the coordinates only, then the system is stable if and only if the potential energy is a minimum at the equilibrium position.

$$K = \frac{[H^+][NO_3^-]p_{NO}^2}{[HNO_2]^3} = 30.1 \text{ M}^{-1} \text{ atm}^2$$

showing the possibility of a forward reaction. A large amount of work on its kinetics was done about half a century ago (see, for instance, Gmelin, volume on N, p. 903-905; Mellor, VIII, p. 459). It appears that the velocity of the isolated forward reaction obeys the equation

$$-\frac{d[HNO_2]}{dt} = v = k \frac{[HNO_2]^4}{p_{NO}}$$

where p_{NO} is the partial pressure in equilibrium with the concentration $[NO]$ in the solution. The rate constant is

$$k = 46 \text{ M}^{-3} \text{ atm}^2 \text{ min}^{-1}$$

Example:

Assume $p_{NO} = 10^{-9} \text{ atm}$ (1 ppb at 1 atm)

and $p_{HNO_2} = 10^{-9} \text{ atm}$

With the appropriate Henry coefficient (see Solubility of HNO_2),

$$[HNO_2] = 4.9 \times 10^{-8}$$

$$v = 46 \frac{(4.9 \times 10^{-8})^4}{(10^{-9})^2} = 2.7 \times 10^{-10} \text{ M min}^{-1}$$

According to this estimate, this possible pathway is entirely negligible.

$$E = \frac{10^{10} \text{ eV}}{10^{10} \text{ eV}} = 10^0 = 1$$

During the evolution of a normal neutron, a large amount of energy is released and some of this energy goes into the kinetic energy of the particles. It is known that the velocity of

the particles increases during the expansion.

$$\frac{10^{10} \text{ eV}}{10^{10} \text{ eV}} = 10^0 = 1$$

where v is the velocity of the particles with the expansion. The ratio is

$$E = \frac{10^{10} \text{ eV}}{10^{10} \text{ eV}} = 10^0 = 1$$

Example:

$$\text{Energy } E_{\text{ph}} = 10^{10} \text{ eV at } t = 1 \text{ sec}$$

$$\text{at } t_{\text{ph}} = 10^{-10} \text{ sec}$$

And the expansion time constant is smaller than

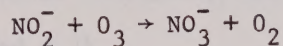
$$t_{\text{ph}} = 10^{-10} \text{ sec}$$

$$E = \frac{10^{10} \text{ eV}}{10^{10} \text{ eV}} = 10^0 = 1$$

Conclusion: In this system, the particle energy is constant.

5. Oxidation of HNO_2 by O_3

A few experiments by Espenson and Taube (1965) showed the possibility of oxidation according to



However, no information was given regarding its rate constant.

Penkett (1972) has found that the velocity of this reaction is

$$v = k [\text{O}_3] [\text{NO}_2^-] \quad k = (1.60 \pm 0.13) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$$

Example

$$\text{Assume } [\text{NO}_2^-] = 10^{-5} \text{ M}$$

$$[\text{O}_3] = 6.5 \times 10^{-10} \text{ M (corresponding to 50 ppb}$$

at 25°C, 1 atm; cf. section on

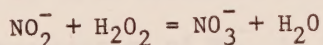
oxidation of SO_2 by O_3 in solution).

$$\begin{aligned} v &= 1.6 \times 10^5 \times 10^{-5} \times 6.5 \times 10^{-10} \\ &= 1.04 \times 10^{-9} \text{ M s}^{-1} = 6.2 \times 10^{-8} \text{ M min}^{-1} \end{aligned}$$

As the example shows, the oxidation rate is negligible.

6. Oxidation of HNO_2 by H_2O_2

This oxidation has been studied by Halfpenny and Robinson (1952), Anbar and Taube (1954) and Edwards and Mueller (1962). The reaction is



2. Calculation of ΔH_f° for H_2O

A few assumptions are necessary and these are listed below the preceding one.

1. ΔH_f° is assumed to be zero.

$$\Delta H_f^\circ = H_f^\circ - H_i^\circ = 0$$

Second, an assumption is made that the heat capacity of H_2O is constant.

Third, (1971) has found that the values of the constants in

$$C_p = a + bT + cT^2 + dT^3$$

4. Results

$$\Delta H_f^\circ = 10.5 \text{ kcal}$$

$$\Delta H_f^\circ = 10.5 \text{ kcal} = 43.9 \text{ kJ}$$

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So the results show, the calculation was in excellent agreement.

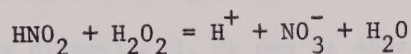
5. Calculation of ΔH_f° for H_2O

This calculation was done by using the following data (1971).

First and last (1971) and second and third (1971). The results are

$$\Delta H_f^\circ = 10.5 \text{ kcal} = 43.9 \text{ kJ}$$

or



The kinetics is not simple. It has been shown to involve the formation of pernitrous acid HOONO . Halfpenny and Robinson find that at low acidities (pH between 4.3 and 4.7)

$$v = k_1 [\text{H}^+] [\text{H}_2\text{O}_2] [\text{HNO}_2]$$

$$\text{with } k_1 = 8.4 \times 10^3 \text{ M}^{-2} \text{min}^{-1} \text{ at } 19^\circ\text{C}$$

for concentrations in the order $[\text{HNO}_2] \sim 10^{-3} \text{M}$, $[\text{H}_2\text{O}_2] \sim 10^{-1} \text{M}$. Obviously, the kinetic equation can also be written

$$v = k_2 [\text{H}^+]^2 [\text{H}_2\text{O}_2] [\text{NO}_2^-]$$

where $k_2 = k_1/K$ and K is the dissociation constant of nitrous acid.

$K \approx 5 \times 10^{-4}$ between 12 and 25°C , so that $k_2 \approx 1.7 \times 10^7 \text{M}^{-3} \text{min}^{-1}$.

Edwards and Mueller find that between pH = 5.0 and pH = 6.7, there is very little dependence of the reaction rate on pH. Near pH = 4.5 the rate increases, presumably by a change in the kinetic path. Between pH 5 and 6.7 they find

$$v = k_3 [\text{NO}_2^-] [\text{H}_2\text{O}_2]$$

$$\text{with } k_3 = 0.034 \text{ M}^{-1} \text{s}^{-1} = 2.04 \text{ M}^{-1} \text{min}^{-1} \text{ at } 25^\circ\text{C}$$

$$k_3 = 0.006 \text{ M}^{-1} \text{s}^{-1} = 0.36 \text{ M}^{-1} \text{min}^{-1} \text{ at } 5^\circ\text{C}$$

In order to obtain an estimate of possible reaction rates, one can take $[\text{H}_2\text{O}_2] = 6 \times 10^{-6} \text{M}$ as estimated in the section on oxidation of SO_2 by H_2O_2 . For the concentration of NO_2^- , it is assumed as an orientation figure,

that $[\text{NO}_2^-]$ is determined by equilibrium with 1 ppb(v) of HNO_2 in the air; most of it will be dissociated, as can be seen from the dissociation constant. For $\text{pH} = 6$, using k_3 , $[\text{NO}_2^-] = 2.5 \times 10^{-5} \text{M}$, and

$$v = 3 \times 10^{-10} \text{ M min}^{-1}$$

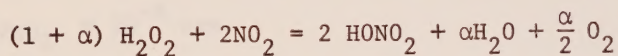
For lower pH, the rate becomes even smaller: at $\text{pH} = 4.3$, ($[\text{H}^+] = 5 \times 10^{-5}$), using k , or k_2 and the corresponding formula, $[\text{NO}_2^-] = 5 \times 10^{-7}$, the result is

$$v = 1.3 \times 10^{-13} \text{ M min}^{-1}$$

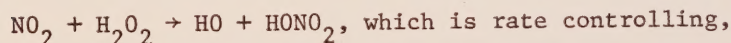
Clearly this pathway for oxidation must be neglected.

7. Heterogeneous oxidation of NO_2 by H_2O_2

Gray et al. (1972) have studied the oxidation of NO and NO_2 by H_2O_2 in gas phase. The H_2O_2 - NO reaction was found to be complex and since it appears to be slower than that between H_2O_2 and NO_2 , reference will only be made to the results of the latter one. The stoichiometry is represented by



where $\alpha < 1$. The mechanism can be represented by



followed by several secondary reactions. The resulting kinetic equation is

$$v = - \frac{d[\text{H}_2\text{O}_2]}{dt} = k [\text{NO}_2] [\text{H}_2\text{O}_2]^n$$

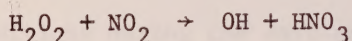
where $0 < n < 1$. The reaction is deemed to occur on the walls, of the container, after adsorption of the reactants. The reaction rate constants can vary from

$$\begin{aligned} k_1 &= (0.5 \text{ to } 1) \times 10^{-18} \text{ cm}^3 \text{ s}^{-1} \\ &= (0.7 \text{ to } 1.5) \times 10^3 \text{ atm}^{-1} \text{ min}^{-1} \quad \text{for } n = 1 \text{ (equivalence} \\ &\quad \text{of units taken at } 25^\circ\text{C)} \end{aligned}$$

to

$$k_0 = 0.71 \text{ min}^{-1} \quad \text{for } n = 0.$$

k_1 would give negligible rates for concentrations such as found in the atmosphere (see Example), but k_0 would correspond to a fast first order reaction with a relaxation time $\tau = 1/k_0 = 1.4 \text{ min}$. Audley et al. (1982) assume that the reaction of NO_2 and H_2O_2 on various surfaces is given by



Example

$$n = 1$$

$$p_{\text{H}_2\text{O}_2} = 10^{-9} \text{ atm}$$

$$p_{\text{NO}_2} = 10^{-8} \text{ atm}$$

$$v = (0 \text{ to } 1.5) \times 10^3 \times 10^{-9} \times 10^{-8} \sim 10^{-14} \text{ atm min}^{-1}$$

Thus the possibility remains that cloud droplets might provide the necessary surface for a fast heterogeneous oxidation of NO_2 by H_2O_2 , transforming most of the NO_2 into HNO_3 in a few minutes, with subsequent

dissolution of the acid into the droplets.⁽¹⁾ Further research is needed to check on that possibility.

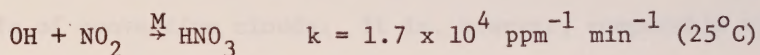
8. Reduction of HNO_2 by SO_2

HNO_2 is a strong oxidant, that may react oxidizing any SO_2 present. This has been considered in the summary on SO_2 oxidation.

F. REACTIONS OF NITROGEN COMPOUNDS IN GAS PHASE

1. Production of HNO_3

HNO_3 can be formed from NO and NO_2 by a number of pathways. However, a kinetic study of the various reactions indicates that under typical photochemical conditions during the daytime, production of nitric acid is dominated by the reaction:



(Orel and Seinfeld, 1977).

The present point of interest is whether the relaxation time for HNO_3 production is comparable, longer or shorter than the cloud

¹ It may be remarked that the aerosol particles may also provide appropriate surfaces for the heterogeneous reaction. However, their surface per unit volume of air is much smaller than that of droplets in a typical cloud. For instance, if there are 10^4 particles per cm^3 (a high content) in the size range corresponding to a radius $\sim 0.1 \mu\text{m}$, the total aerosol surface amounts to $\sim 10 \text{ cm}^2$ per m^3 of air. On the other hand, for a cloud with 300 droplets of radius $\sim 10 \mu\text{m}$ per cm^3 , the total surface amounts to $\sim 3000 \text{ cm}^2$ per m^3 of air.

droplet's life. This can be seen by the following example.

Example:

$$[\text{NO}_2] = 10 \text{ ppb(v)} = 0.01 \text{ ppm}$$

$$[\text{OH}] = 3 \times 10^6 \text{ molecules cm}^{-3}, \text{ equivalent at 1 atm to } 1.1 \times 10^{-7} \text{ ppm}$$

$$\begin{aligned} v &= k [\text{NO}_2] [\text{OH}] = 1.7 \times 10^4 \times 0.01 \times 1.1 \times 10^{-7} \\ &= 1.9 \times 10^{-5} \text{ ppm min}^{-1} \end{aligned}$$

Assuming that $[\text{OH}]$ might remain at that constant level (cf. Weinstock et al., 1980), the relaxation time for oxidation of the NO_2 would be

$$\tau = \frac{1}{k[\text{OH}]} = 606 \text{ min} \approx 10 \text{ hr},$$

This estimate, $\tau \sim 10 \text{ h}$, gives a time constant which is long as compared with the life of convective clouds. It is, however, comparable with that of stratus systems, which may last as long as a few days and where the life time of liquid water is of the order of one day (cf. chapter on mass budgets). It is concluded, therefore, that gas phase HNO_3 production can be ignored in convective clouds, but must be taken into consideration in strati. In both cases, all the HNO_3 present in the air inflow will dissolve into the cloud water, but while in convective clouds no other source need be considered, in strati a continuous production from NO_2 becomes significant, the produced HNO_3 becoming dissolved as soon as it forms.

Example:

Taking as a typical value, 0.7 ppb(v) of HNO_3 and $r_L = 5 \times 10^{-3}$ (liquid water mixing ratio), and recognizing that all the acid will dissociate in solution, the droplets will acquire a concentration

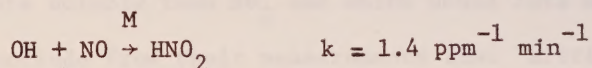
$$[\text{NO}_3^-] = \frac{C_T(v)}{10^{-3} \rho_w^{-1} r_L \mu_a} = \frac{0.7 \times 10^{-9}}{10^{-3} \times 1 \times 5 \times 10^{-3} \times 29}$$

$$= 4.8 \times 10^{-6} \text{ M}$$

In pure water, this would produce an equal concentration of H^+ , giving a $\text{pH} = 5.3$.

2. Production of HNO_2

HNO_2 can also be formed by oxidation with OH:



(Weinstock et al., 1980).

As typical concentrations of NO are of the same order as those of NO_2 , and the rate constant for reaction with OH is similar, it can again be concluded that HNO_2 will not be replenished significantly in the air flowing into a convective cloud if it becomes depleted by dissolution into the cloud water, but may be produced at a significant rate when considering strati. However, unlike the case for HNO_3 , HNO_2 will be dissolved in a proportion that depends on pH (see section on solubility).

G. SUMMARY FOR N OXO COMPOUNDS

According to the previous summary on the relevant reactions of nitrogen oxo compounds, both in the gas and the liquid phase, it appears that no reactions in solution have been found to be capable of producing appreciable amounts of nitric acid. Thus the only important pathway left for the appearance of HNO_3 in cloud droplets seems to be its absorption from the gas phase and perhaps the heterogeneous oxidation of NO_x at the surface of droplets by H_2O_2 .

Nevertheless, the information regarding these compounds is incomplete, and more research is needed in this field.

It is also pertinent to quote the conclusions derived from a field experiment by Lazrus et al. (1983) on warm frontal precipitation in the Ohio River Valley (the Acid Precipitation Experiment: APEX). These authors consider that "possibly NO_2 may be converted in the cloud to NO_3 and N_2O_5 vapors which are much more soluble than NO_2 and which would form HNO_3 in the cloud droplets", and conclude from their measurements that "nitric acid as well as sulfuric acid appears to be generated in clouds, in spite of the low solubility of NO_2 ". This again underlines the need for further research on the in-cloud nitrogen chemistry.

A. DIFFUSION AND SCAVENGING

1. Scavenging of gases in and below the cloud (rainout and washout)

III. PHYSICAL PROCESSES AND SCAVENGING

A. DIFFUSION AND SCAVENGING

1. Scavenging of gases in and below the cloud (rainout and washout)
2. Theory
3. Scavenging parameters
4. Washout of SO_2
5. Washout of O_3
6. Washout of HNO_3
7. Washout of NH_3
8. Washout of H_2O_2
9. Summary of scavenging of gases
10. Aerosol Scavenging
11. Dynamic considerations

B. FREEZING AND SEGREGATION OF SOLUTES

A. DIFFUSION AND SCAVENGING

1. Scavenging of gases in and below the cloud (rainout and washout)

The scavenging of gases by water drops is a complex process involving diffusion in the gas phase of the species considered, transfer through the interface into the drop, and diffusion within the drop. Motion of the drop with respect to the air (gas phase), liquid circulation within the drop and chemical reactions in the liquid must be taken into account. The fundamental theory was developed by Hales (1972). It was thereby shown that the characteristics of the overall process depends on the drop size or size spectrum, the solubility of the gas, its concentration in the gas phase, the mixing process in the drop and the rate of any chemical reactions that may occur. Hales established criteria for limiting conditions that simplify the problem, and the appropriate formulas for each case. Two such limiting conditions are here of special interest.

By "equilibrium washout" it is understood the case when solubility equilibrium between the two phases can be assumed. If solubilization is accompanied by dissociation (as for SO_2 or NH_3), both Henry's law (as corresponding to the bulk partial pressure in the gas) and the dissociation equilibrium constants can be applied. This limiting case is promoted by small drop sizes, low solubilities and low gas concentrations.

"Irreversible" or "total solubility washout" occurs when the species is highly soluble, either because Henry's coefficient is very large or because it becomes mostly ionized in solution so that the dissolved molecular form is present in very low concentration. Large drop sizes will favour this situation. For irreversible washout the partial pressure of the molecular species in the gas is much larger than the equilibrium pressure over the liquid. Thus the gas becomes and remains dissolved, reevaporation being negligible.

These concepts will become clearer by giving some information on the basic theory.

2. Theory

Following Levine and Schwartz (1982), the following equations can be written:

$$F = k_g ([a]_g - [a]_g^*) \quad (1)$$

$$k_g = \frac{D_g}{2R} \left[2 + 0.6 \left(\frac{2Rv}{v} \right)^{1/2} \left(\frac{v}{D_g} \right)^{1/3} \right] \quad (2)$$

$$\frac{d[a]}{dt} = \frac{FS}{V} = \frac{3}{R} F \quad (3)$$

Here

k_g = gas-phase mass transfer coefficient (cm/s)

$[a]_g$ = concentration of species a in the gas, in moles per unit volume

$[a]$ = id. in the liquid phase.

$[a]_g^*$ = equilibrium value, for a given $[a]$

v = falling velocity of drop

v = kinematic velocity of air

D_g = diffusivity of species a in the air (cm²/s)

$\mathcal{R}$ = drop radius

S = drop surface = $4\pi\mathcal{R}^2$

V = drop volume = $(4/3)\pi\mathcal{R}^3$

Equation (1) gives the mass transfer of a from gas to liquid. (2) is

Frossling's equation and (3) indicates the rate of increase of $[a]$.

For simplicity it will be assumed that all the drops are uniform ($\mathcal{R}=\text{const.}$), although the complete theory must take into account the size spectrum. It will also be assumed that the parcel of air considered, with the water drops, can be treated as a closed system. This assumption will be discussed later.

If there are N drops per unit volumes, by mass conservation of a:

$$\frac{d[a]}{dt} \times \frac{4}{3} \pi \mathcal{R}^3 = - \frac{d[a]_g}{dt} \times \frac{1}{N} \quad (4)$$

where $\frac{1}{N}$ is the volume of air corresponding to each drop.

From (4), introducing (1), (3) and the relation $[a] = H^*_{RT} [a]_g^*$ (where H^* is the pseudo-Henry coefficient, or the Henry coefficient if there is no dissociation of $\underline{a}$ in the liquid, and R is the gas constant), it may be obtained

$$-\frac{d[a]_g}{dt} = 4\pi R^2 N k_g ([a]_g - \frac{[a]}{H^*_{RT}}) \quad (5)$$

$$\text{But } [a] = ([a]_{g,0} - [a]_g) \frac{1}{\frac{4}{3}\pi R^3 N} \quad (6)$$

by integration of (4) between $t=0$ ($[a]_0 = 0$) and t , where the subscript o indicates initial value. Introducing this expression into (5) and rearranging, the following first order differential equation is obtained:

$$\frac{d[a]_g}{dt} + \lambda [a]_g = \mu \quad (7)$$

where

$$\lambda = k_g \left[4\pi R^2 N + \frac{3}{R H^*_{RT}} \right]$$

$$\mu = \frac{3 k_g}{R H^*_{RT}} [a]_{g,0}$$

Considering that a is initially totally in the gas phase, the solution of

(7) is

$$[a]_g = \frac{\mu}{\lambda} + ([a]_{g,o} - \frac{\mu}{\lambda}) e^{-\lambda t} \quad (8)$$

This equation indicates an exponential decay of $[a]_g$ from its initial value $[a]_{g,o}$ towards the final value

$$[a]_{g,\infty} = \frac{\mu}{\lambda} = \frac{[a]_{g,o}}{1 + (4/3) \pi \mathcal{R}^3 N_H^* T} \quad (9)$$

with a time constant

$$\tau = \frac{1}{\lambda} = \frac{1}{k_g \left[4\pi \mathcal{R}^2 N + \frac{3}{\mathcal{R} H^* RT} \right]} \quad (10)$$

The initial slope $\{d[a]_g/dt\}_0$ of the decay curve can be calculated from (8) with $\lambda t \ll 1$ or $t \ll \tau$ or from (5) with $[a]_g = [a]_{g,o}$ and $[a] = 0$:

$$\left\{ -\frac{d[a]_g}{dt} \right\}_0 = 4\pi \mathcal{R}^2 N k_g [a]_{g,o} \quad (11)$$

which is independent of H^* (i.e., of the solubility of the gas).

Examination of equation (10) shows that:

$$\text{for } H^* \gg \frac{3}{4\pi \mathcal{R}^3 NRT} = \frac{1}{VNRT},$$

where (VN) is the liquid water content

in mass per unit volume of air,

$$\tau = \frac{1}{4\pi \mathcal{R}^2 N k_g}, \quad (12)$$

independent of H^* ;

$$\text{for } H^* \ll \frac{1}{VNRT}, \quad \tau = \frac{\mathcal{R} H^* RT}{3 k_g}, \text{ proportional to } H^*$$

(13)

According to (9), the final concentration $[a]_{g,\infty}$ remaining in the air varies from 0 for $H^* \rightarrow \infty$ to $[a]_{g,0}$ for $H^* \rightarrow 0$.

This analysis indicates that the general shape of the curves representing $[a]_g$ as a function of time will be such as the two curves schematically plotted in Fig. 1 for two different values of H^* .

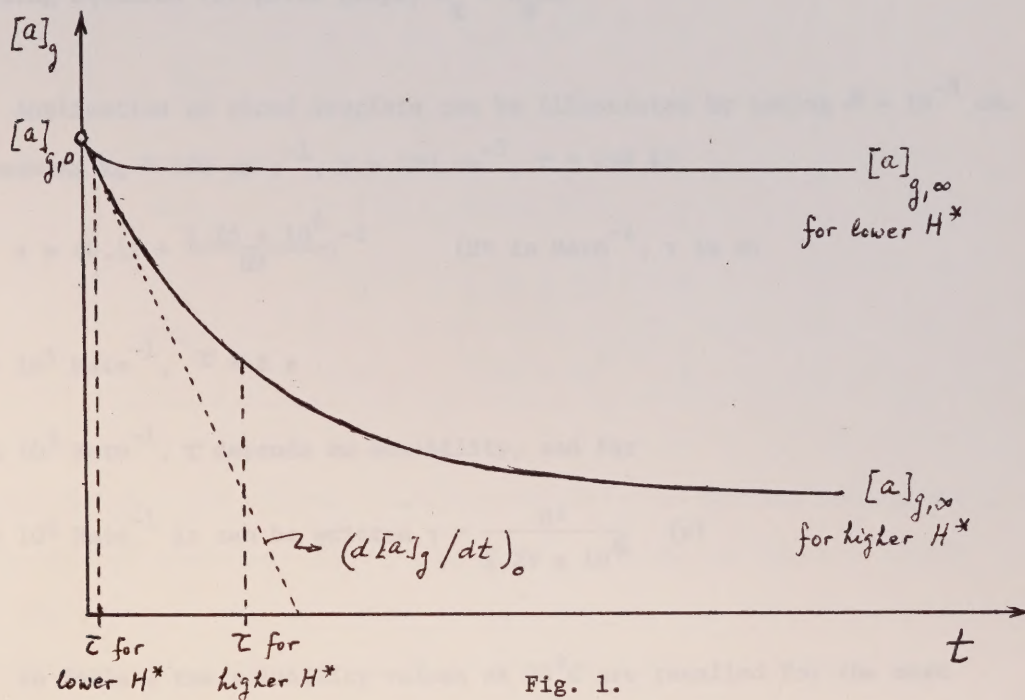


Fig. 1.

The concept of irreversible washout corresponds to the conditions of the initial approximately linear decay in the curves of Fig. 1, i.e. for condition (12), while equilibrium washout corresponds to the final approximately horizontal plateau. It is clear that for $H^* \rightarrow \infty$, the linear part extends down to the horizontal axis.

Rainout and washout are concerned with two widely separated drop size ranges. In the cloud, the gas is dissolved in drops ranging mainly from 5 to 50 μm radius. For raindrops, the size range goes from 0.1 mm to a few mm. This leads to very different situations. The case of cloud droplets will be first considered. In this case the small falling velocity of droplets can be disregarded, and the assumption of closed system appears justified. Furthermore, the Frössling equation (2) gives simply $k_g = D_g/R$.

Application to cloud droplets can be illustrated by taking $R = 10^{-3}$ cm. Then (assuming $k_g \approx 100 \text{ cm s}^{-1}$, $N = 100 \text{ cm}^{-3}$, $T \approx 298 \text{ K}$)

$$\tau = (0.12 + \frac{1.25 \times 10^4}{H^*})^{-1} \quad (H^* \text{ in Matm}^{-1}, \tau \text{ in s})$$

For $H^* \gg 10^5 \text{ Matm}^{-1}$, $\tau = 8 \text{ s}$

$H^* \leq 10^5 \text{ Matm}^{-1}$, τ depends on solubility, and for

$$H^* < 10^4 \text{ Matm}^{-1} \text{ it can be written } \tau = \frac{H^*}{1.25 \times 10^4} \quad (\text{s})$$

In Table 1 the solubility values at 25°C are recalled for the most relevant species in the cloud chemistry of acid rain. H^* coincides with H for the non-dissociating species (O_3 , H_2O_2). For those which dissociate, the calculation has been done for the two pH values delimitating the usual range of observations (3-6). In the last column the time constants are given.

TABLE 1

Species	pH	$H^*(\text{Matm}^{-1})$	$\tau(\text{s})$
O_3	-	1.02×10^{-2}	8×10^{-7}
SO_2	3	2.4×10^1	2×10^{-3}
	6	2.3×10^4	1.5
NH_3	3	1.1×10^8	8
	6	1.1×10^5	4
H_2O_2		9.8×10^4	4
HNO_3	3	3.26×10^9	8
	6	3.26×10^{12}	8

Although the size spectrum was not taken into account, the general conclusions that may be derived from these results are valid. Levine and Schwartz (1982) estimated, for typical convective cloud droplet size spectra, that τ would be $\sim 5\text{s}$ for highly soluble gases. It is clear that solubility equilibrium should be assumed inside the cloud.

The focus of attention will now be displaced to the problem of rain scavenging.

The assumption of closed system in the previous treatment should now be examined. This assumption will still be valid if the drops contained in a given air volume are changing (because drops are falling into it from the top

while others fall out of it through the base) but the drop number concentration and size spectrum is the same, and the concentration of the chemical species studied in the incoming drops is equal to that of the outgoing drops. This is the case when the dissolution time constant is $\tau \gg z_b/v_z$, where v_z is the velocity of the ascending air. This case indicates that there is practically no scavenging below the cloud. (z_b/v_z) is of the order of 10^3 s (17 min) for convective clouds, and of 10^5 s (28 h) for strati.

If, on the contrary, $\tau \ll z_b/v_z$ and H^* is very small (as for O_3) instead of considering a given air parcel, the system analyzed can be one containing the same rain drops (falling from cloud base to ground). The air in which they are contained is changing, but with an essentially constant concentration of the species considered, since this dissolves very little. Then the variable to be considered is $[a]$ rather than $[a]_g$. $d|a|_g/dt$ can be replaced in (5) as a function of $d[a]/dt$, using (4), and $[a]_g$ can be treated as a constant. This result is now

$$\frac{d[a]}{dt} + \lambda' [a] = \mu' \quad (14)$$

with

$$\lambda' = \frac{3k_g}{\mathcal{R}H^*RT}, \quad \mu' = \frac{3k_g [a]_g}{\mathcal{R}}.$$

The solution is of the same type as (8), and the time constant is

$$\tau = \frac{1}{\lambda'} = \frac{\mathcal{R}H^*RT}{3k_g} \quad (15)$$

This equation applies in the cloud (for H^* small), as well as for rain washout in the case. In fact it coincides with (13), which was explained to be valid in a cloud.

When τ is comparable to z_b/v_z a more complex model should be considered for washout, with both air and drops changing concentrations as a function

of height, while moving in countercurrent. This will not be treated here.

3. Scavenging parameters

Two different parameters have been used to describe the effect of scavenging. One of them is the dimensionless washout ratio W defined as

$$W_a = \frac{[a]_l}{[a]_g} \quad (16)$$

where a is the chemical species, $[a]$ is its concentration in moles per unit volume, and the subscripts l and g refer to the liquid and gas phase, respectively. By using Henry's coefficient and making the appropriate transformation of variables, it can be seen that for equilibrium conditions,

$$W_a = RTH_a \quad (17)$$

where H must be substituted by H^* (pseudo-coefficient) if there is dissociation in the water.

The other parameter is the scavenging coefficient Λ , which is defined assuming that the rate of decrease of concentration in the air $-d[a]_g/dt$ due to scavenging is proportional to the concentration:

$$-\frac{d[a]_g}{dt} = \Lambda[a]_g$$

or

$$[a]_g = [a]_{g,0} e^{-\Lambda t} \quad (18)$$

This is a simplified version of (7) (with Λ identified as λ), when μ can be put ≈ 0 (H^* very large). It is clear that attention should be made as to whether Λ is applied as a constant (as defined in (17) or (18)) within the right range of conditions.

The time constant is $\tau = 1/\Lambda$. This first order process corresponds to the condition of irreversible scavenging from a box or layer being depleted from species a by either cloud droplets or raindrops. As explained before, Λ depends on the size spectrum of the drop, particularly on its lower limit sizes. It does not depend on the chemical species, except through the diffusion coefficient in air D_g , which varies little from one species to another.

A relation can be established between W and Λ . If P is the rainfall rate in $\text{kg/m}^2 \cdot \text{s}$, L is the liquid water content in mass per unit volume of air and v_p is the falling velocity of drops,

$$P = Lv = L \frac{\Delta z}{\Delta t} \quad . \quad (19)$$

Applying (17) with the approximation $d/dt \approx \Delta/\Delta t$

$$-\frac{\Delta[a]_g}{\Delta t} = \Lambda[a]_g \quad . \quad (20)$$

If $[a] = 0$ at the top of Δz , and $[a]$ represents the value at the base of Δz ,

$$-\Delta[a]_g = \frac{L}{\rho_w} \Delta[a] = \frac{L}{\rho_w} [a]$$

(ρ_w = density of water), or

$$-\frac{\Delta[a]_g}{\Delta t} = \frac{L[a]}{\rho_w \Delta t}$$

(21)

Comparing (20) and (21), introducing L from (19) and the definition of W , the relation

$$\Lambda = \frac{PW}{\rho_w \Delta z}$$

or

$$\Lambda = \frac{PW}{\Delta z} \quad (22)$$

if P in mm/h, is obtained.

4. Washout of SO_2

This has been discussed on the basis of various models by a number of authors: Hales (1972, 1978), Barrie (1978, 1981), Beilke and Gravenhorst (1978), Carmichael and Peters (1979). Altwicker and Chapman (1981) have made an experimental check of the theoretical treatments used by the previous authors; they found that the first three overestimate the SO_2 absorption (by factors between 4 and 6), while Charmichael and Peters underestimate it (factor ~ 10). Further studies have been done by Baboolal et al. (1981) and Walcek et al. (1981).

The type of process occurring with SO_2 depends on its concentration.

Hales (1978) indicates that for a distance beyond 20 stack heights of a point source, the concentration is sufficiently low for equilibrium scavenging to occur. As this study is concerned with widespread pollutants rather than concentrated plumes, the assumption can be considered valid in all cases.

Barrie (1981) has calculated the washout ratio W for SO_2 , as a function of the rain pH. His results are plotted in Fig. 2. It may easily be seen that the two limiting lines are given by the formula

$$\log_{10} W = \log_{10} (K_1 H RT) - \log_{10} |H^+| = a + pH, \quad \text{with} \quad \begin{aligned} a &= 0,35 \text{ at } 0^\circ\text{C} \\ a &= -0,30 \text{ at } -25^\circ\text{C} \end{aligned}$$

(K_1 = first dissociation constant)

Knowing W , the rate of precipitation P ($\text{kg/m}^2 \cdot \text{s}$) and the concentration of SO_2 in the lower layers of air above the ground, the mass flux density of SO_2 washed out and carried to the ground by rain F ($\text{kg/m}^2 \cdot \text{s}$) can be easily calculated:

$$F = W P [SO_2]_a = W P \frac{P}{RT} C_{SO_2}(v) = W P \frac{\mu_a P}{\mu_{SO_2} RT} C_{SO_2} \quad (23)$$

If P is given in "mm/hr", the expression (23) must be multiplied by 3600. Using (17), equation (23) could be also formulated as

$$F = P H^*_{SO_2} C_{SO_2}(v) \quad p = P H^*_{SO_2} p_{SO_2} \quad (24)$$

The rate of oxidation of SO_2 in the raindrops will be generally small enough to neglect its consideration in the process of washout.

It will be noticed that the influence of NH_3 and any eventual

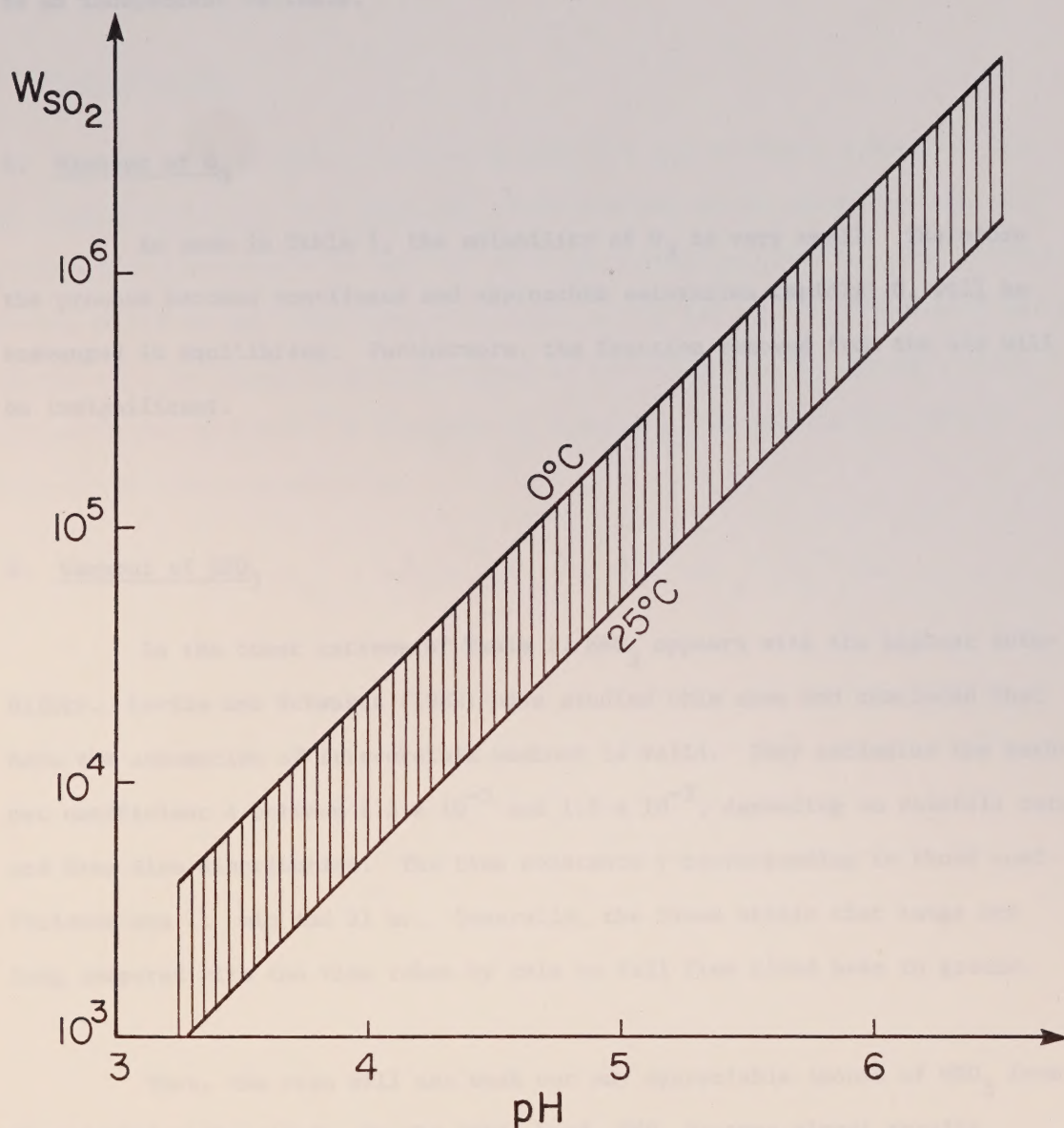


Fig. III.2 - The dependence of the washout ratio of SO_2 by rain on pH for two temperatures, 0 and 25°C, under equilibrium scavenging conditions (the hatched area represents those situations commonly encountered in the atmosphere) (From Barrie, 1981).

alkalinity of the cloud condensation nuclei, as discussed in the chapter on equilibrium conditions, is implicit in the value of pH, which is here treated as an independent variable.

5. Washout of O_3

As seen in Table 1, the solubility of O_3 is very small. Therefore the process becomes non-linear and approaches saturation rapidly; O_3 will be scavenged in equilibrium. Furthermore, the fraction removed from the air will be insignificant.

6. Washout of HNO_3

In the other extreme of Table 1, HNO_3 appears with the highest solubility. Levine and Schwartz (1982) have studied this case and concluded that here the assumption of irreversible washout is valid. They estimated the washout coefficient Λ between 1.3×10^{-5} and 1.5×10^{-3} , depending on rainfall rate and drop size distribution. The time constants τ corresponding to those coefficients are 11 min and 21 hr. Generally, the times within that range are long compared with the time taken by rain to fall from cloud base to ground.

Thus, the rain will not wash out any appreciable amount of HNO_3 from the air below the cloud. On the other hand, HNO_3 becomes almost totally dissolved in the cloud droplets, and once these are caught by raindrops the liquid will retain the acid until reaching the ground. This consideration is valid for an all-water process; if riming on ice particles is involved, HNO_3

will probably be largely restored to the air by segregation.

7. Washout of NH_3

Perusal of Table 1 indicates that this gas is highly soluble in the pH range of interest. For the usual concentrations in the atmosphere one must expect that washout will be very far from equilibrium conditions. For instance, taking pH = 6 as the least favourable case, an initial concentration of 10 ppb(v) in the air will become totally dissolved in cloud droplets, producing a total concentration of 7×10^{-5} M (assuming $r_L = 5\text{g/kg}$). The equilibrium partial pressure of such a solution is

$$p_{\text{NH}_3} = \frac{7 \times 10^{-5}}{H^*} \approx 6 \times 10^{-10} \text{ atm} \ll 10^{-8} \text{ atm}$$

It may be estimated that for raindrops of ~ 1 mm radius and rainfall rate of ~ 1 mm/hr, τ will be in the order of 1 hour. Therefore rain arrives to the ground essentially with the concentration acquired by cloud water, and the washout will be an irreversible first order process. The conclusions are as for HNO_3 .

8. Washout of H_2O_2

The same argument as above can be repeated - with the same figures - in this case, for which H has practically the same value as $H_{\text{NH}_3}^*$ at pH = 6. As 10 ppb(v) can be considered an upper limit for usual atmospheric concentrations of H_2O_2 , and lower concentrations would give washout conditions ever further away

from equilibrium, the case of H_2O_2 is again like that of HNO_3 .

9. Summary of Scavenging of Gases

As a summary, the following results can be stated:

1. Inside the cloud, solubility equilibrium can be assumed between cloud droplets and air, at all times.
2. Washout of O_3 can be neglected, due to its low solubility.
3. Washout of the highly soluble H_2O_2 , NH_3 and HNO_3 can be neglected, due to the long time constant. These species are transported by rain to the ground with their concentrations in the cloud, close to the base.
4. Washout of SO_2 occurs in equilibrium, with a washout ratio W that can be estimated as a function of pH and temperature.

10. Aerosol Scavenging

This is a complex field, combining rainout and washout and implying a number of different processes. A summary has been given by Pruppacher and Klett (1978, Section 12.7). Scavenging of aerosol in general and sulfates in particular has been the object of particular attention by, among others, Hales (1978), Garland (1978) and Scott (1982).

The following is an enumeration of the different mechanisms leading to the capture of aerosol:

1. Nucleation of cloud drops. The cloud drops form by absorption of water by hygroscopic nuclei. The nuclei that become so activated are called the cloud condensation nuclei (CCN) and constitute a fraction of the atmospheric aerosol that depends on the water vapour supersaturation reached by the ascending air. This is discussed elsewhere (cf. Chapter IV). CCN are particles of equivalent radius $\geq \sim 0.1 \mu\text{m}$.
2. Convective diffusion. This is the process of Brownian diffusion enhanced by the relative motion of water drops with respect to air.
3. Thermophoresis and diffusiophoresis. The particles in the air are subject to forces associated with thermal and concentration gradients, such as exist in the proximity of growing or evaporating drops.
4. Turbulent shear and turbulent inertial capture.
5. Gravitational or inertial capture.

To this listing one should still add consideration of the effects of electric charges and fields. Processes 2 and 3 are more important for smaller particles ($< 0.1 \mu\text{m}$) in the cloud (large surface to volume ratio in the droplets), while 4 and 5 only become important if the particle is large enough ($\geq \sim 1 \mu\text{m}$).

Garland (1978) has made a comparison of the contribution of the various mechanisms to the net deposition of particulate sulfate. He found that by far the greatest contribution was the rainout of CCN. In second term

washout by gravitational capture could be important if the aerosol has an appreciable fraction of large particles. Brownian diffusion in the cloud can also contribute a minor fraction. Convective diffusion by rain and phoretic effects can be neglected.

Whatever the mechanism, as any particles actually colliding with a drop remain adhered ("sticking coefficient" = 1) and eventually dissolve or become embedded in it, the collection of particles by water drops is comparable to the irreversible washout of gases, and can be represented by the formula

$$-\frac{d[m]_g}{dt} = \Lambda_a [m]_g \quad (25)$$

where $[m]_g$ is the concentration of aerosol in the air, in mass per unit volume, and Λ_a is defined as the scavenging coefficient for the aerosol (either for a given class of particles, or a mean value for the total aerosol). Λ_a depends on the drop size spectrum and the precipitation rate.

Considering the variation of Λ_a with the size of aerosol particles and with the size of scavenging drops, it is found that (Pruppacher and Klett, 1978, p. 395):

1. The variation of Λ_a with the particle size presents a strong broad minimum starting around $0.1 \mu\text{m}$, and up to $1 \mu\text{m}$ radius, if the process 1 is not considered. This corresponds to particles too big to be affected by Brownian motion and too small to be accreted efficiently by impaction. Process 1 (rainout of CCN) will at least partially compensate this gap (the "Greenfield" gap).
2. There is also a minimum of scavenging efficiency for drop radii of about 200 to $300 \mu\text{m}$.

From both theoretical considerations and field observations, it is found (see Pruppacher and Klett, 1978, p. 396) that the overall Λ_a for the whole aerosol is in the range of 10^{-3} to 10^{-4} s^{-1} , i.e., corresponding to a time constant of around 1h.

Garland (1978) finds that a washout ratio W of 300 is typical of most elements, but nitrate and sulfate yield values of about 1000. Or, in terms of scavenging coefficient, $\Lambda_a \sim 10^{-4} \text{ s}^{-1}$ for sulfate. Scott (1982), making estimates appropriate for representing the average scavenging from features like large rainbands or frontal systems, found that Λ_a could be represented by the formulas

$$\Lambda_a = 0.88 P \quad (\text{h}^{-1}) \quad \text{for snow precipitation}$$

$$\Lambda_a = 1.26 P^{0.78} \quad (\text{h}^{-1}) \quad \text{for rain, at temperatures} > 0^\circ\text{C}.$$

P is the precipitation rate, in units of mm h^{-1} . He estimates that the uncertainties in Λ_a are within a factor of 6 for snow, and within a factor of 2 or 3 for rain.

It should be remarked that P is a function of altitude, which depends on the rate of precipitation growth within the cloud. Scott (1982) considered this problem and calculated two typical curves $P = f(z-z_b)$ for summer and winter conditions.

Finally, it may be remarked that these estimates apply to the scavenging of sulfates and nitrates, of particular interest because of their relations to the corresponding acids, but also to CaCO_3 in regions where this is abundant. The latter type of aerosol may have a strong neutralizing effect on the acidity of precipitation (cf. Munger, 1982). Some indication about the

aerosol present in the air feeding the cloud may be obtained if the previous trajectory of that air mass can be traced back the type of soil over which it has travelled can be determined. Distribution of the different types of soil in North America can be found in The National Atlas of the U.S.A. (1970) and in Clayton et al. (1977).

11. Dynamic considerations

When considering convective clouds, the updrafts feeding the cloud will transport air from the mixed layer. The aerosol and SO_2 concentrations will be those prevailing uniformly in that layer. The equilibrium washout of SO_2 will be determined by pH of the precipitation and temperature, and the mass flux transported to the ground can be calculated with formulas (23) or (24), with the $[\text{SO}_2]_g$ of the mixed layer (i.e., as measured close to the ground), for the area covered with precipitation.

The case of stratiform clouds is different in that no mixed layer will be present, so that the profile of $[\text{SO}_2]_g = f(z)$ or $C_{\text{SO}_2} = f(z)$ between ground and cloud base has to be taken into account. Assuming that the influx of air into the cloud comes uniformly from the whole layer below the cloud, the influx of SO_2 will be given by

$$M \overline{C_{\text{SO}_2}} = \frac{M}{p_o - p_b} \int_{p_b}^{p_o} C_{\text{SO}_2} dp \quad (26)$$

where M is the air influx and p_o and p_b are the pressures at ground and cloud base, respectively. The transport of SO_2 to the ground by rain will be given by formula (23) or (24), with the concentration of SO_2 at the ground, since the rain is assumed to be in constant equilibrium.

B. FREEZING AND SEGREGATION OF SOLUTES

When ice grows out of an aqueous solution, the solutes contained in the liquid phase are rejected, up to a certain extent, by the growing ice crystal lattice. If the ice continues to grow, the concentration of solutes increases close to the interface, and a concentration gradient sets up from the interface toward the bulk of the liquid, unless the liquid is stirred by some mechanism up to the interface itself.

There is a sudden change of concentration as one goes from one side to the other of the interface. A segregation coefficient S has been defined as the ratio of the concentration in the solution over that in the ice, across the interface:

$$S = \frac{[\text{solute}]_{\text{water}}}{[\text{solute}]_{\text{ice}}}$$

The theory of the process has been considered by Jaccard and Levi (1961), who also made measurements for HF. DeMicheli and Iribarne (1963) made measurements for a dozen of different electrolytes, including acids and bases; values of S ranged from 5 to 628. A few other measurements were done before by other workers. It is clear that the segregation coefficient reflects the greater or smaller inadequacy of the solute molecules (or ions) to fit as an impurity into the crystal lattice of the ice.

Except perhaps for nondissociated NH_4OH , none of the measurements above mentioned refer to neutral molecules. The experiments were done in each case with a plane ice surface, with the ice growing orderly from a

solution which was either stagnant or well stirred up to the interface.

A similar phenomenon should occur in a cloud, when supercooled droplets freeze. The ice growth in this case will have different characteristics, probably with ice crystals shooting through the droplet and then growing until the whole drop is frozen. If the solute is nonvolatile, as for instance H_2SO_4 or a salt, segregation will certainly make its final concentration in the ice highly nonuniform, but all the solute will remain in the frozen particle. On the other hand, if the solute can pass to the gaseous phase as a gaseous molecule, as for instance SO_2 , HNO_3 or NH_3 , segregation will be followed by diffusion through the liquid and transfer through the drop surface to the surrounding air. Iribarne et al. (1983) studied the loss of SO_2 from supercooled drops (-10°C) of 0.5 to 1 mm diameter during freezing and found that it amounted to $\sim 75\%$; i.e. the frozen drops retained about one quarter of the SO_2 dissolved. Although some doubt exists about the extrapolation of these figures to cloud size droplets, there are reasons to believe that the rate-determining step in the loss sequence is the segregation itself rather than diffusion; in that case it is likely that the result can be applied to cloud droplets. In any case, 25% may be considered as a maximum figure for the retention of SO_2 . No other measurements have been made for other compounds.

This type of process will be operating in the development of precipitation by the freezing (Bergeron-Findeisen) mechanism, and will affect all the mass of precipitated water, except the part accreted by the molten particles below the level of 0°C . Obviously, it will not apply to the "warm rain" mechanism.

IV. MASS BUDGETS

Variables and symbols used

A - Air budget

1. Stratus
2. Stratus with embedded band structure
3. Convective clouds - Entrainment
4. Fronts

B - Water budget

1. Liquid water mixing ratio in a saturated adiabatic ascent
2. Entrainment
3. Freezing
4. Radiative exchanges
5. Life time of cloud droplets and of liquid water
6. Droplet size spectrum
7. Precipitation

C - Budget of various chemical species

1. Input
2. Dissolution and scavenging in the cloud
3. Chemical reactions
4. Freezing effects
5. Output

IV. MASS BUDGETS

In this chapter a general analysis will be made of the mass budgets of air, water substance and chemical compounds, as they appear for the various cloud and precipitation systems. In so doing, the main complications and difficulties will be pointed out, as well as the necessity for simplifications and possible ways of performing them.

Variables and Symbols Used

The following definitions and symbols will be adopted:

M = air mass flux (mass of air flowing per unit time)

M_c = air mass flux density (mass of air per unit time and unit area) averaged over the total cloud region area
($= \sigma \rho w_c$, where w_c is the average vertical velocity and σ is defined below)

A_c = area of a cloud

A = cloud covered area, in the whole region

A_p = area covered by precipitation

$\mathcal{A}$ = total area covered by the system

σ = fractional area covered by clouds. $\sigma = A/\mathcal{A}$

P = rate of precipitation = mass of water substance per unit area and unit time. Italic capitals will indicate integration over the time duration $\mathcal{T}$ of the system; e.g.

$$\mathcal{P} = \int_0^{\mathcal{T}} P \, dt$$

Subscript b will be used consistently to indicate the base of the cloud, and subscript t to indicate the top of either the cloud or the region being considered.

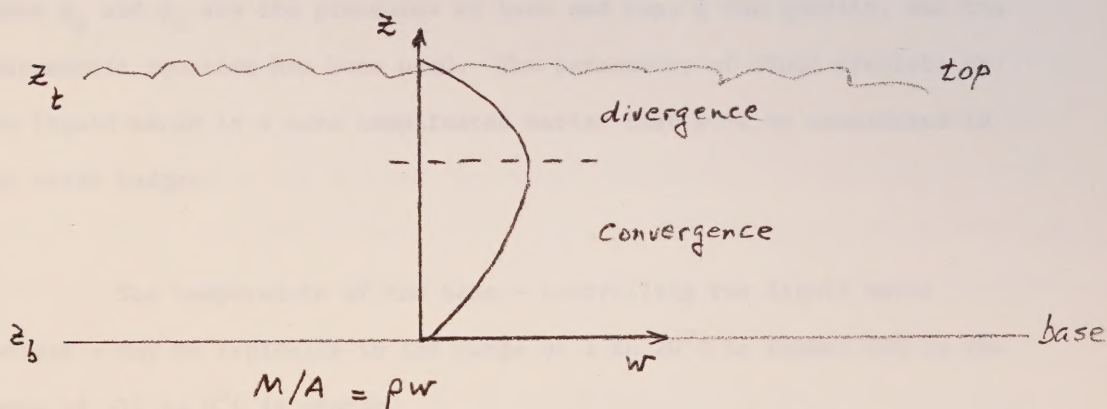
Obviously, if r is the water vapour mixing ratio, c_i the mass mixing ratio of chemical species i , etc., rM will be the mass flux of water vapour, $c_i M$ the mass flux of species i , etc.

A - AIR BUDGET

The various types of systems will be considered in order.

1. Stratus

In this case the base of the cloud covers the whole area under consideration: $A \equiv \mathcal{A}$. The influx is considered of uniform density: $M/A = \text{const}$. The situation can be summarized in the following sketch:



w is here the vertical velocity, which will have a profile along the height such as indicated in superimposed curve, and ρ is the air density.

The air from below the cloud will enter the cloud through the base, will generally ascend through the cloud in a spiraling trajectory and emerge through the cloud borders aloft, in the divergence region.

Values of the vertical velocity w are typically in the order of the cm/s, and precipitation rates in the order of a fraction of mm/h.

The total life of the system may vary from a fraction of a day to several days and during that time it may be considered in a stationary state. Any air parcel coming into the stratus may remain in it for a time of the order of one day. Thus strati may provide long times for any in-cloud chemistry. If $\mathcal{M}$ is the total mass of a cloud of area A_c and M_c the air mass flux density feeding it, the average permanency of the air inside the cloud will be given by

$$\tau = \frac{\mathcal{M}}{A_c M_c} = \frac{p_b - p_t}{g M_c}$$

where p_b and p_t are the pressures at base and top, g the gravity, and the hydrostatic equation has been used. The permanency of cloud droplets or the liquid water is a more complicated matter that will be considered in the water budget.

The temperature of the base - controlling the liquid water content - may be typically in the range of 1 to 20°C in summer and in the range of -15 to 0°C in winter.

For the in-cloud chemistry, three different situations must be distinguished: the cloud consists only of water, only of ice, or partly water and partly ice. The effect on the chemistry will obviously be quite different for the three cases.

2. Stratus with embedded band structure

This case is similar to the previous one, except for the nonuniformity of the stratus, presenting rain-producing bands with higher ascending velocities, in the range of 0.1 to 1 m/s. The precipitation rate P may be in the range of the mm/hr.

Apart from the effect of precipitation, the in-cloud chemistry will be different for the area outside bands, which provides a much longer residence time for a smaller influx of pollutants, and for the 'rainbands' area, where the influx is larger and the permanency shorter.

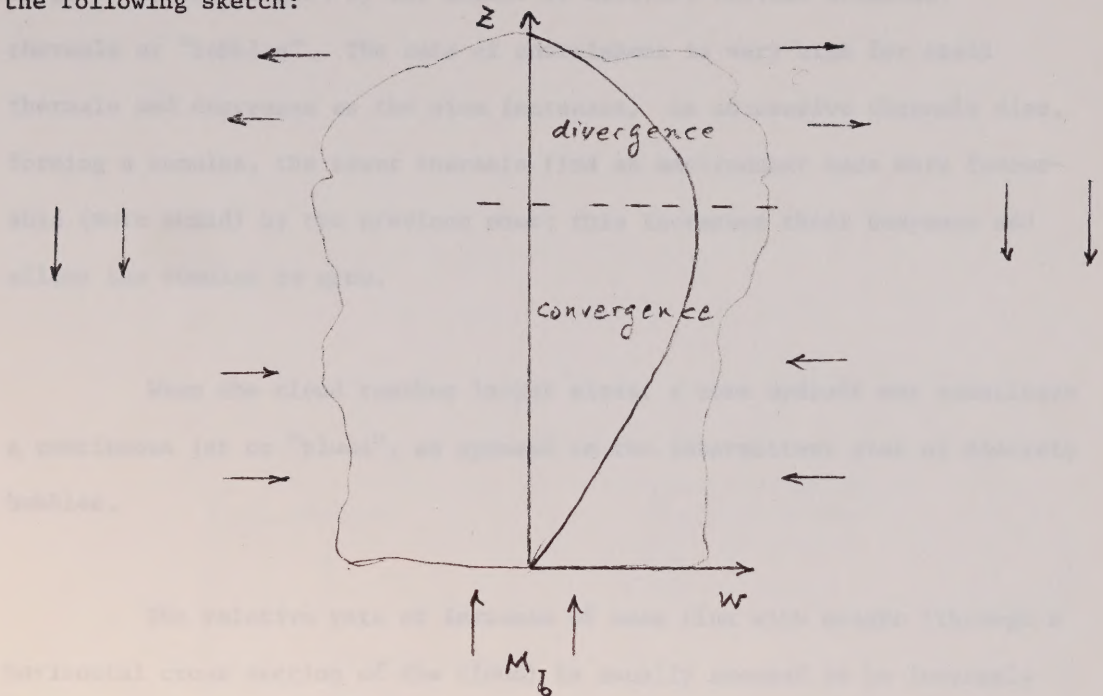
3. Convective clouds - Entrainment

These systems are considerably more complicated in various respects. The individual components (Cu, Cb) are highly time-dependent, passing through growing, maturity and decay stages; they are highly turbulent, with extreme variability of their significant parameters (vertical velocity, liquid water content, etc.) throughout their cross sections; and the amount of lateral air inflow (entrainment) is difficult to estimate. Thus drastic simplifications are unavoidable if the effect of these systems on the redistribution and transformation of pollutants is to be considered in a quantitative or semi-quantitative way.

The duration of individual clouds may be in the order of the hour, although upper region residues (of water or ice) may remain for longer times. Updrafts and downdrafts are in the order of meters per second.

The general characteristics of the air flows can be summarized in

the following sketch:



The figure indicates the vertical velocity profile superimposed to the cloud. The total influx of air is composed of the ascending air through the base M_b and the lateral entrainment M_e . The compensating subsidence around the cloud has the effect of providing M_e with air characteristics of higher levels, and therefore generally purer and drier; this permits one to consider that it contains no pollutants and that its water vapour mixing ratio can be neglected.

The rate at which external air is incorporated into a convective cloud (entrainment) is extremely variable and depends on various factors. It is difficult to estimate and the formulas proposed are only supported by relatively few measurements.

Convection may take two main forms. Except for clouds of very

large size, cumuli grow by the ascent of discrete buoyant elements: thermals or "bubbles". The rate of entrainment is very high for small thermals and decreases as the size increases. As successive thermals rise, forming a cumulus, the newer thermals find an environment made more favourable (more humid) by the previous ones; this increases their buoyancy and allows the cumulus to grow.

When the cloud reaches larger sizes, a core updraft may constitute a continuous jet or "plume", as opposed to the intermittent rise of discrete bubbles.

The relative rate of increase of mass flux with height (through a horizontal cross section of the cloud) is usually assumed to be inversely proportional to the cloud radius:

$$\alpha \equiv \frac{1}{M} \frac{dM}{dz} = \frac{b}{R} \quad .$$

b is a constant which can be related to the half-broadening angle θ of either a thermal or a jet. Laboratory estimates of b range from $b = 2\theta = 0.2$ for a jet to $b = 3\theta = 0.6$ for a thermal. b has also been estimated as high as 0.75 (see Cotton, 1975, a and b). It has also been found that the best values of b depend not only on the characteristics of the clouds, but also on whether liquid water content or the height of the cloud is the parameter to be predicted. Cotton concludes that a single adopted value of b can only represent "a restricted portion of the cloud life cycle such as the active stage of cloud growth and to a narrow range of meteorological and geographical conditions" (1975a). Fig. 1 (reproduced from Cotton, 1975b) compares

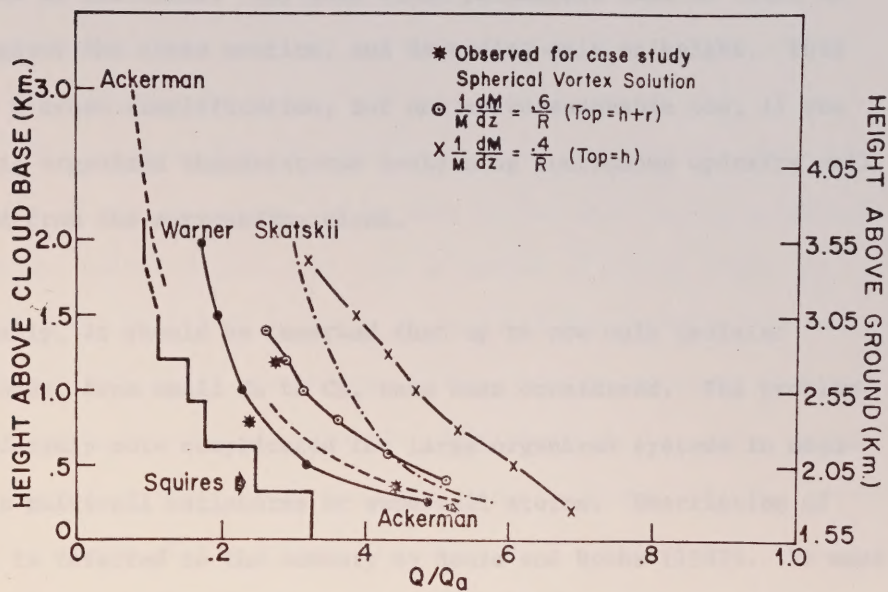


Fig. IV.1 The ratio of the mean liquid water content at a given height above cloud base to the adiabatic value [from Cotton, 1975].

the values of the liquid water content from various observations (including a case study) (Q) with the adiabatic value (Q_a) as a function of height.

Thus, for example, if b is taken as 0.4, a cumulus with 5 km radius will have its air flux $M(=M_b + M_e)$ increased by 8% per km, while for a small cumulus of 1 km radius, the increase will be $40\% \text{ km}^{-1}$. This, as has been shown, has a very large effect on the liquid water content, as well as on the dynamics of the cloud. Any such cloud parameters will be taken as uniform throughout the cross section, and depending only on height. This is admittedly a crude simplification, but not an unreasonable one, if one excepts the big organized thunderstorms containing continuous updrafts well differentiated from the surrounding cloud.

Finally, it should be remarked that up to now only isolated convective clouds, from small Cu to Cb, have been considered. The problem becomes considerably more complicated for large organized systems in meso-scale, such as multicell hailstorms or supercell storms. Description of these systems is referred to the summary by Houze and Hobbs (1982). It must also be recognized that, due to their large dimensions and intensity of the air flows, these systems must be exceptionally active in the redistribution of pollutants in the troposphere.

4. Fronts

Cloud and precipitation systems associated with fronts fall in the categories of St with rainbands and convective clouds (Cu, Cb). Therefore, being here concerned with their effect on chemistry, they will not be further discussed.

B - WATER BUDGET

The influx of water substance is given by the air influx through the base of the cloud (M for a St, M_b for a convective cloud) multiplied by the water vapour mixing ratio of the air: $M r$. The mixing ratio is of course the saturation mixing ratio at the temperature of the base: $r = r_w(T_b)$.

As the air rises above the cloud base, a small supersaturation will occur, with the result of activating the cloud condensation nuclei and forming droplets around them. As the ascent proceeds, the supersaturation increases by the adiabatic expansion, and more nuclei are activated. At a certain level, the condensation of vapour will start reducing the supersaturation in spite of the expansion, and no more nuclei will become activated. This initial phase occurs within some tens of meters of ascent (see, for instance, Mason 1971, p. 197 ff.); thus, practically from the base of the cloud, the droplet population, depending on the aerosol characteristics and the updraft velocity, becomes established. From there on, the water vapour continues condensing on the already-existing droplets, whose size increases. In any case, the amount of liquid water available for chemical reactions in solution per unit mass of air will increase with height, towards a limiting value given by total condensation of the existing water vapour.

This general description corresponds to the simplest situation and may correspond to a stratus cloud or, ideally, to the core updraft in a cumulonimbus. In convective clouds, where mixing with dry external air occurs, part of the liquid water being formed must re-evaporate to saturate the entrained air; the liquid water may eventually disappear altogether (top of the Cu).

If the cloud is sufficiently developed vertically, the liquid water will become entirely glaciated when it reaches a temperature of -40°C . Ice nuclei are also active at higher temperatures, and this may lead to glaciation at lower levels.

The outfluxes of water substance will be: cloud droplets that emerge from the cloud and evaporate into surrounding air, ice crystals undergoing the same process, and precipitation to the ground either as liquid or solid.

The significant parameter giving the liquid water content is the liquid water mixing ratio, designated by r_L . In what follows, the variation of r_L with height will be considered. This will be done first for the simpler case of a saturated adiabatic ascent, and then the effect of entrainment in convective clouds will be analyzed.

1. Liquid water mixing ratio (r_L) in a saturated adiabatic ascent

The temperature of the cloud base is the critical input parameter determining the values of r_L . If the ascent can be considered adiabatic (no mixing with external air), r_L can be calculated as a function of height z or of pressure p . Most conveniently, a tephigram (or other equivalent aerological diagram) gives direct readings; starting with the point representative of the cloud base (T_b, p_b), the saturated adiabat is followed toward lower pressures, and at each level p the saturation water vapour mixing ratio r_w can be read (as well as the temperature T). By difference with the value at the cloud base, the liquid water mixing ratio is obtained:

$$r_L = (r_w)_b - r_w$$

If it is desired to have r_L as a function of the height above the cloud base ($z - z_b$), the following formula can be used for an approximate numerical integration:

$$\Delta z = \frac{R_a \bar{T}}{g_0} \ln \frac{p_1}{p_2}$$

where Δz is the difference of height of the (relatively close) isobars p_1, p_2 , R_a is the specific gas constant for air, $g_0 = 9.80665 \text{ m s}^{-2}$ and $\bar{T}$ is the average absolute temperature of the layer Δz (cf. Iribarne and Godson, 1981, p. 172). This integration neglects a relatively small difference of temperature between the ascending parcel and the environment (the difference that confers buoyancy to the parcel); this may cause errors $< 3\%$ in Δz .

As an example, calculations have been made for a cloud with the

base at $p_b = 800$ mb. Table 1 gives the temperature $T(^{\circ}\text{C})$, saturation mixing ratio r_w (g/kg) and height above the base $(z-z_b)$ (km) as functions of the pressure, for several cloud base temperatures T_b . Fig. 2 shows the corresponding saturated adiabat as a heavy curve on a tephigram.

With the numerical results displayed in Table 1, the graphs of Figs. 3-6 can be readily plotted. Fig. 3 gives the saturation mixing ratio r_w as a function of height over the base, for clouds with $p_b = 800$ mb and various T_b . Fig. 4 gives a similar plotting for the resulting liquid water mixing ratio r_L . Figs. 5 and 6 plot the same variables, but as a function of pressure rather than height.

For the purpose of parameterization, the curves of Fig. 6 could be approximated by straight lines such as indicated, corresponding to the formula

$$r_L = a (p_b - p) \quad .$$

The values of the coefficient a (for r_L given in g/kg and the pressure in mb) are plotted in Fig. 7 as a function of T_b . This curve corresponds to $p_b = 800$ mb, but it is an easy matter to produce other curves for various other values of p_b (e.g. 950, 900, 850, 750, 700 mb) and plot them together. a can then be found easily for any particular case, by interpolation.

TABLE 1

Variation of r_w , T and $(z-z_b)$ for a cloud with base at $p_b = 800$ mb.

T_b (°C)	- 10			0			10			20		
	r_w (g/kg)	T (°C)	$z-z_b$ (km)	r_w (g/kg)	T (°C)	$z-z_b$ (km)	r_w (g/kg)	T (°C)	$z-z_b$ (km)	r_w (g/kg)	T (°C)	$z-z_b$ (km)
P (mb)												
800	2.24	-10.0	0	4.80	0	0	9.7	10.0	0	18.8	20.0	0
700	1.30	-17.7	1.01	3.30	-7.0	1.05	7.5	4.3	1.10	15.9	15.3	1.14
600	0.78	-27.4	2.14	1.90	-15.2	2.23	5.3	-2.5	2.33	13.0	10.0	2.42
500	0.26	-38.5	3.42	0.94	-25.7	3.58	3.2	-11.3	3.75	9.8	3.2	3.91
400	-	-	-	0.32	-39.4	5.15	1.5	-23.2	5.42	6.3	-5.7	5.69
300	-	-	-	-	-	-	0.38	-40.3	7.45	2.9	-18.8	7.89

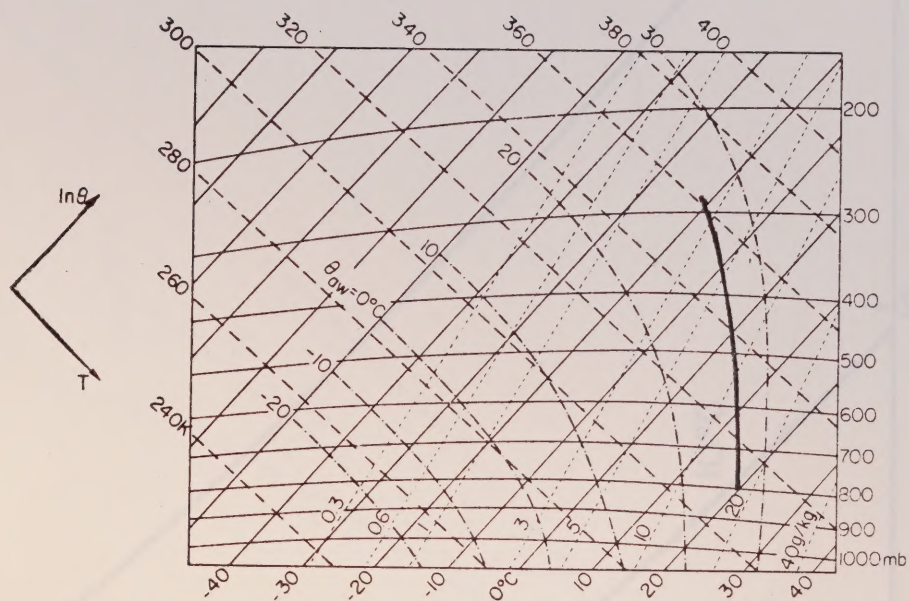


Fig. IV.2 - Saturated adiabat (thick curve)
 passing through $p_b = 800$ mb,
 $T = 20^{\circ}\text{C}$, drawn on a tephigram.

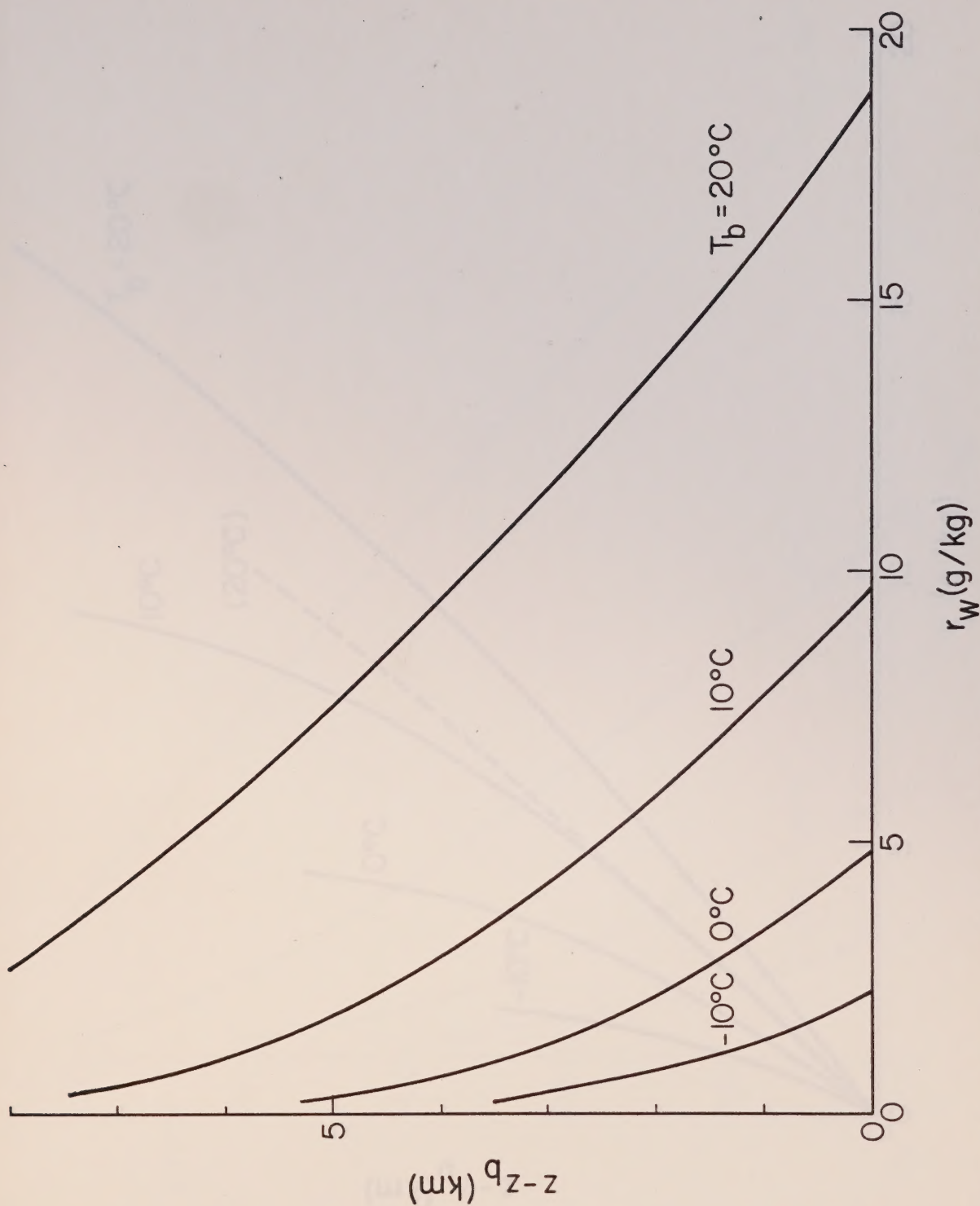


Fig. IV.3 - Variation of the saturation mixing ratio r_w with height, along saturated adiabats passing at $P_h = 800$ mb through various values of T_h .

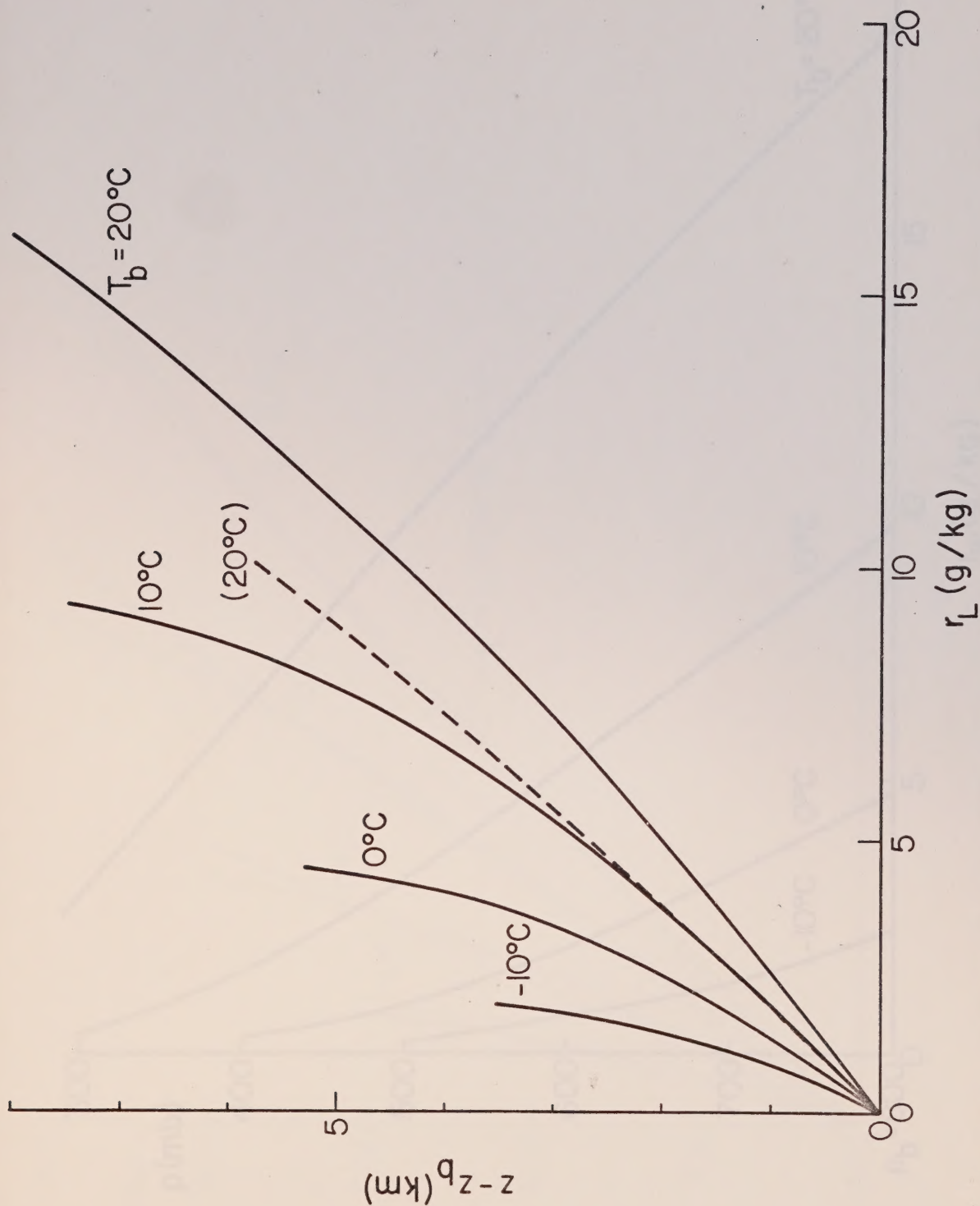


Fig. IV.4 - Variation of the liquid water mixing ratio r_L with height, for clouds with the base at $p_B = 800$ mb and various temperatures T_b . The dashed curve corresponds to $T_b = 20^\circ\text{C}$, for a

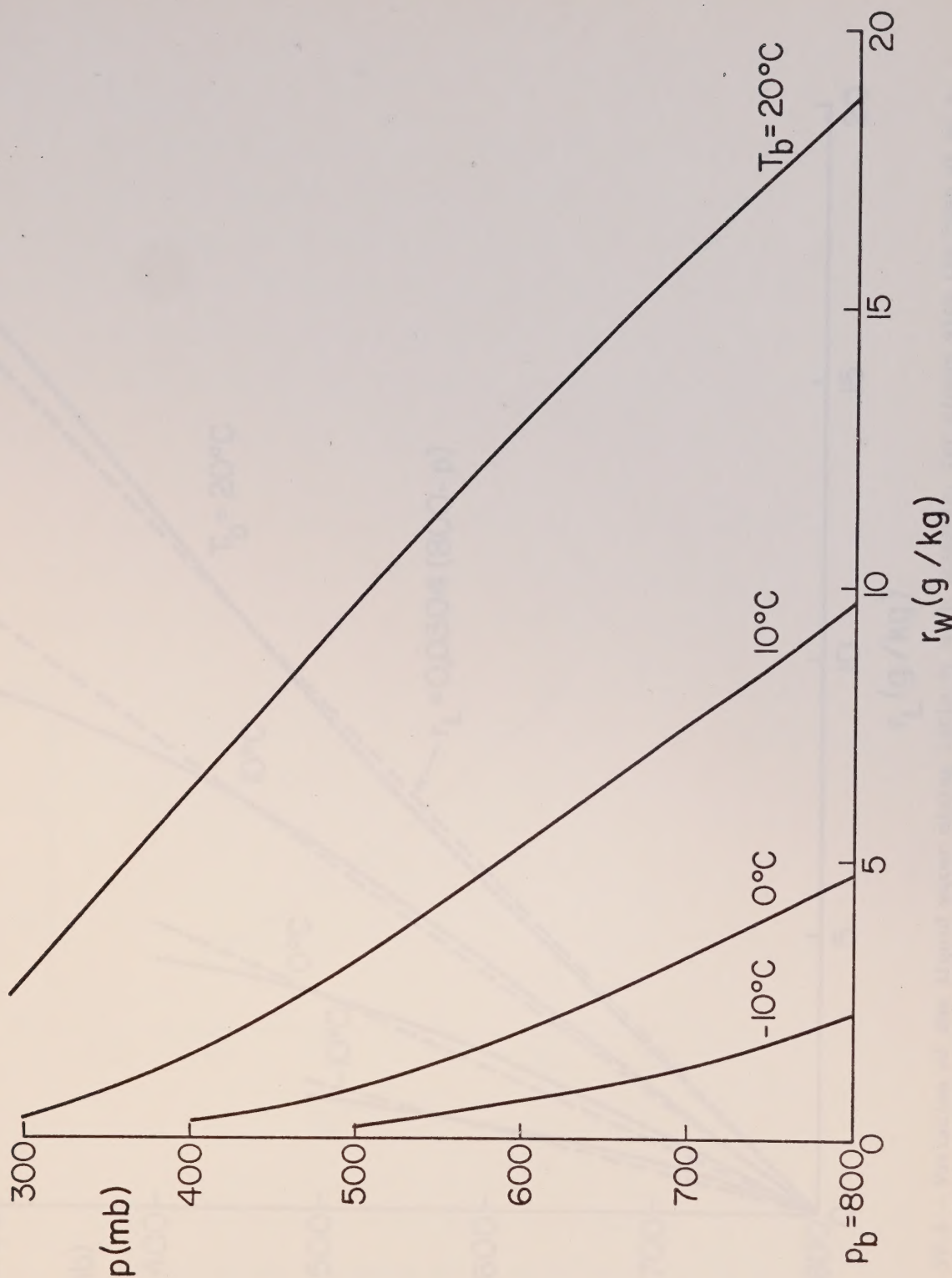


Fig. IV.5 - Variation of the saturation mixing ratio r_w with pressure, along saturated adiabats passing at $p_b = 800$ mb through various values of T_b .

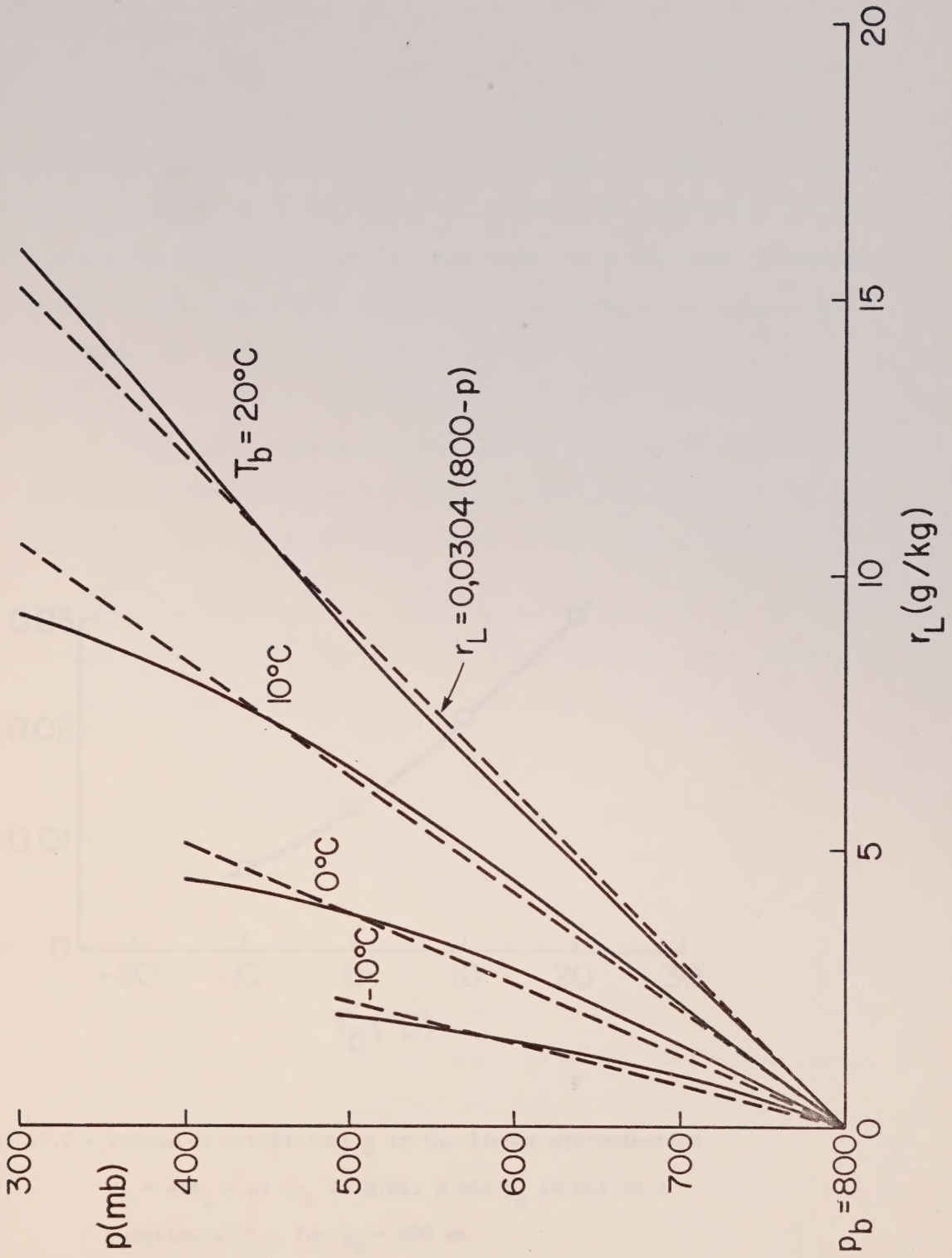


Fig. IV.6 - Variation of the liquid water mixing ratio r_L with pressure, for clouds with the base at $p_b = 800$ mb and various temperatures T_b . The dashed lines are linear approximations for the curves.

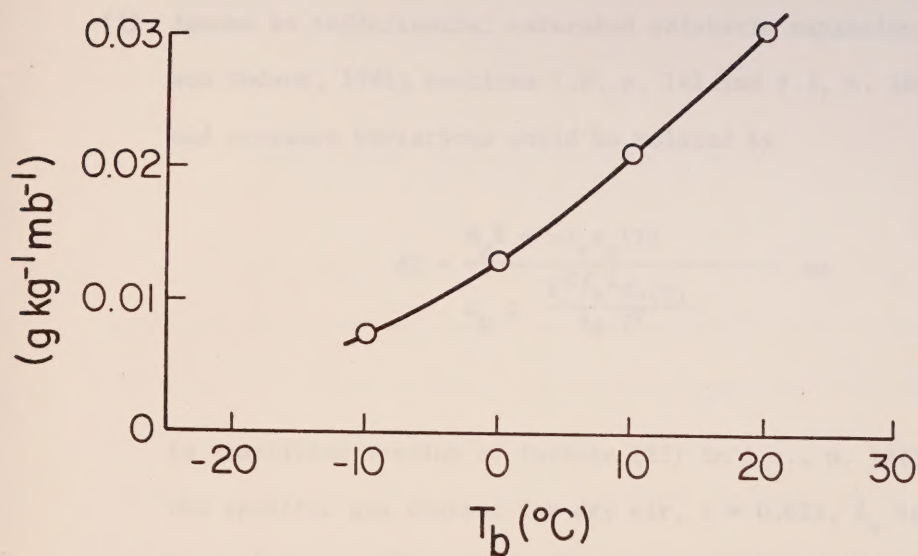


Fig. IV.7 - Values of coefficient a in the linear approximation

$r_L = a(p_b - p)$ (r_L in g/kg , p and p_b in mb) as a function of T_b , for $p_b = 800 \text{ mb}$.

2. Entrainment

The previous curves have been derived for the case of adiabatic ascent. No mixing with the environment is assumed. This is adequate for an extended stratus, but is certainly a poor approximation for convective clouds, unless these have developed to the stage of cumulonimbus and the curves refer to the core updraft. Entrainment must therefore be considered in many cloud systems, with the corresponding modification of parameter estimates.

The proper treatment of entrainment, provided the simplifying hypothesis of uniform parameters throughout the cross section of the cloud is accepted, could be developed according to the following steps:

- (1) Assume an infinitesimal saturated adiabatic expansion (cf. Iribarne and Godson, 1981; Sections 7.8, p. 141 and 9.3, p. 180). Temperatures and pressure variations would be related by

$$dT = \frac{R_d T + \epsilon \ell_v e_w(T)}{c_p p - \frac{\epsilon^2 \ell_v^2 e_w(T)}{R_d T^2}} dp$$

(a simplified version of formula (23) in l.c., p. 181). Here R_d is the specific gas content for dry air, $\epsilon = 0.622$, ℓ_v is the latent heat of evaporation, e_w is the saturated vapour pressure at temperature T , and c_p is the specific heat capacity of air at constant pressure.

(2) A fractional mass

$$\alpha dz = - \frac{\alpha}{g\rho} dp$$

of dry external air is mixed into the cloud. This dilution with dry air decreases both the water vapour mixing ratio $r_w(T) = \frac{\varepsilon e_w(T)}{p - e_w(T)}$ and the liquid water mixing ratio r_L by a factor $(1 - \frac{\alpha}{g\rho} dp)$. The temperature will change according to the rates of horizontal (isobaric) mixing (l.c., Section 7.4, p. 127). Because of the decrease in water vapour mixing ratio, the air becomes unsaturated.

(3) The air is brought again to saturation by isenthalpic evaporation of part of the liquid water (l.c. Section 7.3, p. 123). The approximate formula

$$dT = - \frac{\ell_v}{c_p} dr$$

(r = water vapour mixing ratio) applies here.

Thus the liquid water mixing ratio decreases not only by the saturated adiabatic expansion (as when there is no entrainment: step 1) but also by dilution (step 2) and evaporation (step 3). The complete analytical treatment of the process, however, becomes too complicated and laborious, and the drastic simplifications (uniform cloud cross section, choice of α) do not warrant it. Instead, an approximate treatment can be made with the help of a tephigram, as described in Iribarne and Godson (1981), Section 9.9, p. 195; it is based on decomposing the process into three steps described above, for finite ascents Δp or Δz (rather than dp or dz) of, say, 1 km each. An example will be given for illustration.

A cloud with the base at $p_b = 800$ mb, $T_b = 20^\circ\text{C}$ will be considered. The relation between z and p can be obtained from the data in Table 1. It will be assumed that entrainment adds 4% of air through each km of ascent. After the first kilometer over the base, when the temperature has reached the value $T_1 (= 16.0^\circ\text{C})$, 0.04 kg. of external air are mixed with each kg of cloud air. The decrease in temperature produced depends on the temperature of the external air; if this is 2 K lower than the cloud air, the mixing will decrease T by 0.08 K (new value = T_2) and the mixing ratio by 0.6 g/kg. The liquid water mixing ratio, which after step 1 is 2.5 g/kg (cf. Fig. 4) has been reduced by the dilution in the amount of 0.1 g/kg. Step 3, to saturate the air at its new temperature T_2 can be obtained from

$$T_2 + 2500 r = T_3 + 2500 r_w(T_3)$$

or from the graphical procedure, to give the final temperature T_3 and mixing ratio r_w . It is found that the amount of water evaporated (decrease in r_L equal to the increase in vapour from r to $r_w(T')$) is 0.5 g/kg. Thus, the final result is a liquid water mixing ratio 0.6 g/kg lower than in the absence of entrainment. The whole procedure can be repeated for successive finite ascents of 1 km each, and a curve of $r_L = \int(z)$ obtained; such a curve (slightly depending on the temperature and humidity profile of external air) is represented as a dashed curve in Fig. 4; an equivalent curve could be plotted as a function of pressure, in Fig. 6.

3. Freezing

All the previous considerations assume that the condensed water is in liquid state. A general limitation is given by the temperature of -40°C , below which all water is frozen. Some icing will occur at lower

levels, starting around -15°C (this depends on the ice nuclei population) and increasing with height. The cloud may remain, however, predominantly a water cloud up to the glaciation level at -40°C . In stratiform clouds with small ascending velocity, glaciation may propagate downward, following ice crystal precipitation, converting the cloud above the level of 0°C in an ice cloud (cf. Mason, 1971, p. 306 ff.). These circumstances should be taken into account in the applications to in-cloud chemistry.

4. Radiative exchanges

Usually, radiative energy exchanges are very slow compared with the vertical motions leading to cloud systems in the atmosphere. Exchanges in the "long wave" region (i.e., in the terrestrial and atmospheric range of wave lengths, from 4 to several tens of micrometers) between a cloud and other horizontal layers, the ground or space, can cause temperature changes of the order of 1 or 2 degrees per day. While this becomes appreciable for stratiform clouds with very slow ascending motions, lasting one or two days, it is still a marginal effect which will not be considered.

5. Life time of cloud droplets (τ_{cd}) and of liquid water (τ).

As explained before, cloud droplets are formed on activated cloud condensation nuclei within a short distance above the base of the cloud. The droplet population is then established, and water vapour will condense on the existing droplets, causing them to grow, rather than forming new droplets. In a stratiform cloud, the life of a droplet (τ_{cd}) will be the time taken from its formation near the base to its exit aloft. In convective clouds, the situation is more complicated, because there exist simultaneously rising masses of air, downdrafts and other regions more or less stagnant.

However, the important parameter providing the time during which dissolved chemical species have remained in aqueous solution and had the opportunity of reacting (as, for instance, is the case of the oxidations of SO_2 in liquid phase), is not the duration of a drop but the permanency of each mass element of liquid water (τ). This parameter is highly variable and difficult to assess, particularly for convective clouds.

If the ascending motion is uniform, as in a stratus, the life of each differential amount of liquid water will be given by the time taken from its condensation until its exit from the cloud and evaporation or its precipitation as part of precipitation particles. As water condenses gradually, according to the curves of Fig. 5, there will be continuous spectrum of values for the life time τ .

The situation is not so simple for convective clouds. These clouds grow by successive ascent of thermals that become mixed with the surrounding air. In the cloudy environment thus formed, new thermals rise. This intermittent process continues until, if the convection is strong enough, a continuous updraft jet is formed. During the process, most of the volume of the cloud will be turbulent, but relatively stagnant with respect to the ascending motion; i.e., the average vertical velocity is close to 0 in large

regions of the cloud. Downdrafts will also be present, less important than the updrafts during the development stage, but becoming predominant during the dissipation stage. Thus it is obvious that for a large fraction of the liquid water mass, the permanency can be of the same order of the life of the cloud; while for other portions the life time can be much shorter; also, some portions will become part of precipitation from the cloud.

6. Droplet size spectrum

The droplet size spectrum will depend on the nature of the aerosol, and therefore on the type of air mass. It is well known that maritime air masses contain a comparatively higher concentration of large nuclei, and this leads to fewer and larger drops in the cloud. Continental air masses, on the other hand, lead to smaller droplets in higher concentrations. As air masses in Eastern Canada can have various origins, this is a variable characteristic that depends on each particular situation. However, the droplet size spectrum is not of primary importance. It can only have an influence on the concentration of soluble substances coming from the nuclei and on some processes involving capture by diffusion of certain species from the air (cf. Chameides and Davis, 1982).

7. Precipitation

Two different mechanisms for the initiation of precipitation within

the cloud are recognized as operative in different conditions. The "warm rain" process occurs entirely in liquid phase, with the drops growing first by condensation and then by accretion. The "ice" or "Bergeron-Findeisen" process implies freezing of a fraction of the supercooled droplets on ice nuclei, growth of the ice by condensation and then by accretion of supercooled droplets, and eventually melting into rain drops below the 0°C level. Although the limiting conditions under which one or the other process becomes predominant are not clearly defined, it is generally admitted that in middle to high latitudes, as corresponding to eastern Canada, precipitation is originated by the ice process. Thus, precipitation will start at some temperature between 0°C and -40°C (for instance around -15 to -20°C , where enough ice nuclei may become active). The particles will rise in the ascending air until their falling velocity overcomes the air vertical velocity, and then will fall within the cloud. As they fall, their size increases and so does the precipitation rate through lower and lower horizontal surfaces. This precipitation will be of ice particles (snow crystals, graupel or hail) above the 0°C level, and will become of rain drops shortly below that level. (If hail particles are large enough, they will arrive still solid to the ground.)

According to this brief description, it would be necessary, for a complete understanding of the water balance within the cloud, and also for a detailed calculation of the effect of scavenging, to know $P = P(z)$ (where P is the precipitation rate). This, however, is a difficult problem involving a detailed knowledge of the cloud microphysics, which is usually unavailable and in any case cannot easily be generalized. Parametric approximations are possible, although still rather complex to perform. Scott (1982) has developed such an approximation. His expression for rain fall rate P within the cloud and up to the 0°C level may be written

$$P(z) = P_b - 1.13 \times 10^{-16} \bar{w} (z - z_b)^{4.55}$$

where P is given in mm/h, P_b is the value at the cloud base, which in general will differ little from the value at the ground, and $\bar{w}$ is the average value between cloud base z_b and height z of the liquid water content given in g/m^3 . A somewhat less simple procedure is given to estimate the snow precipitation rate above the 0°C level. Much more extensive studies were already made in this complex field by Kessler (1969).

On the following page, Scott's Fig. 3 and Table 1 are reproduced. The figure shows the curves of $P = P(z)$ obtained for winter and summer conditions as indicated in the table. Straight lines have been superimposed on Scott's curves to indicate that a simple linear growth may be a reasonable first approximation; this approximation would be equivalent to assume that the mass of precipitation falling through the cloud base has its origin uniformly distributed between the base and the top of the straight line. Or, in other words, that the rate of conversion from cloud water to precipitation is uniform throughout the whole layer.

C - BUDGET OF VARIOUS CHEMICAL SPECIES

This section refers to the different processes involved in the mass balances of various chemical species (other than water), whether they are considered pollutants or not. Most of these processes are treated in detail in other chapters (on equilibrium, chemical reactions, scavenging, etc.). Thus the aim of this section is only to present a summary of the transfers and transformations that a given compound undergoes in a cloud

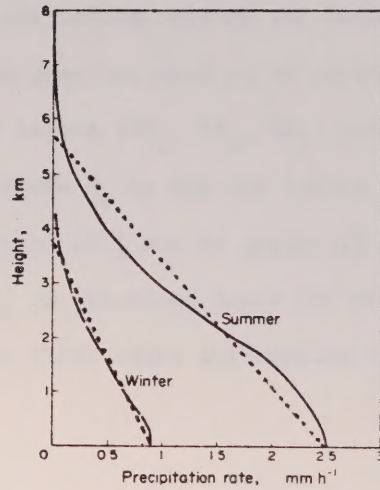


Fig. 3. Precipitation rate as a function of height.

Table 1. Data used to generate curves in Fig. 3

	Summer storm	Winter storm
Cloud top (km)	8.0	4.7
Freezing level (km)	4.6	0.3
Mean cloud water below H_f (g m^{-3})	0.30	0.04
Mean cloud water above H_f (g m^{-3})	0.70	0.07

(H_f : height of 0°C level)

system.

1. Input

If c_i is the mass mixing ratio of species i , its influx into the cloud will be $M c_i$ for stratus (where M is the air influx) and $M_b c_i$ for a cumulus (where M_b is the air influx through the base). Air incorporated by entrainment above the base does not need to be considered when i is mainly concentrated in the lower layers (SO_2 , NO_x , NH_3 , aerosol, etc.). On the other hand, a term $M_e c_i$ (where M_e is the air influx by entrainment) should be added if the concentration of i may be appreciable above the mixed layer (e.g., O_3). Obviously, c_i in the mixed layer (if there is one) or c_i as a function of height, is the first basic information needed to study the evolution of i .

From the influx just mentioned, a term should be subtracted: the washout or scavenging by precipitation below the cloud. This is considered in the chapter on scavenging. As is then shown, this term is negligible for a number of species (O_3 , NH_3 , H_2O_2 , NNO_3) but important for SO_2 . Obviously, a knowledge of the area A_p covered by precipitation (which will be a fraction σ of the cloud area A) is necessary to estimate the amount of SO_2 lost by the air feeding the cloud and subtract it from the total input.

2. Dissolution and scavenging in the cloud

As soon as an air parcel has entered the cloud, any gaseous species is in a two phase system, and will tend to a solubility equilibrium. That such an equilibrium is rapidly reached has been shown elsewhere (III.2); the time constants involved are no longer than a few seconds, and may be much shorter.

It is essential to recognize the requirements of mass conservation in this process. If the chemical species is not produced by reaction in the cloud, its amount in an air parcel is limited to the initial content in the incoming air and there is no transport mechanism to replenish it. Thus very soluble gases (such as H_2O_2 or NH_3) virtually disappear from the gas phase, while others (like O_3) will remain mainly gaseous. This requirement has been taken into account throughout this study.

As regards the aerosol, the particles become incorporated into the drops by activation of cloud condensation nuclei and by Brownian motion. This is considered in the chapter on scavenging.

3. Chemical reactions

Once within the cloud, chemical reactions that may occur both in gaseous and liquid phase constitute sources or sinks of certain compounds. Thus photochemical oxidation of SO_2 constitutes a sink for SO_2 and a source of H_2SO_4 . Oxidation of SO_2 in aqueous phase constitutes a sink for SO_2 and H_2O_2 or O_3 , and a source of H_2SO_4 . These transformations are essentially the subject of the chapter on in-cloud chemistry.

4. Freezing effects

The equilibrium between gaseous and aqueous phases becomes disturbed when freezing occurs, either by glaciation or by accretion of supercooled droplets onto ice precipitation particles. The effect on dissolved gases is discussed in the section on freezing segregation.

V. PARAMETERIZATION

1. Continuity equations

2. Liquid water

3. Chemical species

a) SO_2

b) H_2O_2

c) O_3

d) HNO_3

e) NO_2

f) The term $[A]$

g) H^+

h) NH_3

4. Precipitation pH

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PARAMETERIZATION

In this chapter an analysis will be made on how the knowledge summarized in the previous chapters could be incorporated parametrically into models describing the effect of cloud systems on the redistribution and transformation of pollutants. This is done in a general way, and no attempt is made to propose a particular model. It is clear that, in view of the complexity of the problem, any tractable models must by necessity introduce numerous simplifications; see, for example, Hales (1982).

1. Continuity equations

In order to formulate a parameterized calculation of the processes occurring within the cloud, the starting point is given by the continuity equations describing mass conservation for liquid water and for the different chemical species.

$$\frac{DX}{Dt} + X \nabla \cdot \vec{v} = S \quad (\text{kg m}^{-3} \text{ s}^{-1}) \quad (1)$$

where X is the concentration, in mass per unit volume of air, of the species considered, DX/Dt is the substantial or convective derivative

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{v} \cdot \nabla \quad (2)$$

$\frac{\partial}{\partial t}$ is the local derivative, and S is a term or terms representing all the sources (terms > 0) and sinks (terms < 0) of X .

Alternatively, total mixing ratios $C_{i,T}$ can be used instead of the concentrations X_i in mass per unit volume. The relation between the two types

of variables is trivial:

$$X_i = \rho C_{i,T}$$

where ρ = air density.

2. Liquid water

The dynamic model, including the equations of motion, energy and continuity, will provide a solution for the temperature T . The water vapour mixing ratio can then be directly calculated from

$$r = r_w(T, p) \quad (3)$$

where the subscript w indicates saturation. Condensation to liquid water, which constitutes a source term, can then be expressed as

$$-\frac{Dr_w}{Dt} = -\frac{\partial r_w}{\partial T} \frac{DT}{Dt} + \frac{\partial r_w}{\partial p} \frac{Dp}{Dt}$$

or, considering that X is referred to the unit volume of air,

$$S_1 = -\rho \left(\frac{\partial r_w}{\partial T} \frac{DT}{Dt} + \omega \frac{\partial r_w}{\partial p} \right) \quad (4)$$

A sink term must be added in precipitating clouds, to account for the disappearance of cloud droplets either as supercooled droplets in the riming of ice precipitation particles or as droplets coalescing with rain drops. This conversion of cloud water into precipitation is a complex phenomenon quite variable with the conditions in the cloud (cf. Kessler, 1969, p. 37 ff) and therefore it does not lend itself to any detailed generalization. In chapter IV it was suggested that the rate of increase of P with decreasing height might be approximated by a linear function.

The sink term is

$$S_2 = \frac{dP}{dz} \quad (5)$$

(P decreases with z). If the approximation by a linear function is used

$$P = k(z_{pt} - z) \quad (6)$$

where z_{pt} is the height of the top of the precipitation region, or the level at which the precipitation is assumed to be originated (which might be, say, the level of -15 or -20°C). At $z = z_b$ (cloud base), P is the precipitation falling through the cloud base, which can in general be taken as the precipitation rate measured at the ground P_o (except for a rain of fine droplets that might experience considerable evaporation). Thus

$$S_2 = -k = -\frac{P_o}{z_{pt} - z_b} \quad (7)$$

where P_o is given in $\text{kg m}^{-2} \text{s}^{-1}$.

The complete term S is

$$S = S_1 + S_2 \quad (8)$$

3. Chemical species

Regarding chemical species i other than water, X will represent the total concentration of the species, both in gas phase and in solution in the cloud water, referred to the unit volume of air. Because, as has been discussed in reference to diffusion and scavenging, solubility equilibrium according to Henry's law can be assumed valid at all times

$$[i] = H_i^* C_i(V) \quad p = \frac{\mu_a}{\mu_i} H_i^* C_i \quad p \quad (9)$$

(where $H^* \equiv H$ for non-dissociating species); having solved the continuity equation for X , it is a trivial matter to derive the fraction in gas phase and the fraction in solution. Therefore, for these species

$$X_i = \rho(C_i + 10^{-3} \rho_w^{-1} \mu_i \bar{r}_L [i]) \quad (10)$$

(ρ_w in g cm^{-3}). The two concentrations C_i and $[i]$ can then be calculated (using (9) and (10)) from

$$C_i = \frac{X_i}{\rho(1 + 10^{-3} \rho_w^{-1} \mu_a \bar{r}_L H_i^* p)} \quad (11)$$

$$[i] = \frac{X_i H_i^* p}{\rho \left(\frac{\mu_i}{\mu_a} + 10^{-3} \rho_w^{-1} \mu_i \bar{r}_L H_i^* p \right)} \quad (12)$$

However, in many cases the situation becomes simpler in that either the species is very little soluble (O_3) and therefore the second term on the right hand side of (10) can be ignored, or it is very highly soluble (HNO_3 , H_2O_2 , NH_3) and the first term in (10) can be ignored.

The terms S for the different species that must be considered should take into account the chemical reactions producing them (sources) or consuming them (sinks), both in gas and aqueous phase, and the rainout (sink).

Considering a reaction in gas phase occurring at the rate $v_{i,\text{gas}} = \pm d[i]_g/dt$, where $[i]_g$ is the concentration in moles of i per unit volume of air and the sign is + for production and - for consumption, the source (or sink) term will be

$$S_{\text{gas}} = \mu_i v_{i,\text{gas}} \quad (13)$$

For a reaction in solution $v_{i,\text{aq}} = \pm d[i]/dt$ (where $[i]$ is the molarity),

$$S_{\text{aq}} = 10^{-3} \rho_w^{-1} \rho \mu_i r_L v_{i,\text{aq}} \quad (14)$$

Regarding rainout, as seen in the chapter on scavenging, neither O_3 (because of its low solubility) nor the ^{scavenging of} very soluble gases (because of their long time constants) need to be considered. Only the scavenging of SO_2 between 0°C and z_b by the rain must be taken into account; this will be considered below.

a) SO_2

It has been seen in the section on SO_2 oxidation in gas phase that this may be assumed to occur with a rate

$$v_{\text{gas}} = - \frac{d[SO_2]}{dt} = - 1.2 \times 10^{-6} [SO_2]_g \quad (\text{mol m}^{-3} \text{s}^{-1})$$

or

$$v_{\text{gas}} = - 1.2 \times 10^{-6} \frac{\mu_{SO_2}^p}{RT} C_{SO_2}(v) = - 1.2 \times 10^{-6} \frac{\mu_a^p}{RT} C_{SO_2} \quad (\text{kg m}^{-3} \text{s}^{-1}) \quad (15)$$

For v_{aq} , appropriate expressions might be

$$v_{\text{aq}} = - \frac{d[HSO_3^-]}{dt} = - k_{H_2O_2} [HSO_3^-] [H_2O_2] [H^+] - k_{O_3} [O_3] [HSO_3^-] [H^+]^{-0.4} \quad (16)$$

with $k_{H_2O_2} = 3.1 \times 10^9 \text{ Mmin}^{-1} = 5.2 \times 10^7 \text{ M s}^{-1}$

$$k_{O_3} = 1.074 \times 10^6 \text{ M}^{-0.6} \text{ min}^{-1} = 1.79 \times 10^4 \text{ M}^{-0.6} \text{ s}^{-1}$$

if Penkett et al.'s data are used for O_3 ; or

$$v_{aq} = -k_{H_2O_2} [HSO_3^-] [H_2O_2] [H^+] - k'_{O_3} [O_3] [HSO_3^-] [H^+]^{-0.85} \quad (17)$$

$$\text{with } k'_{O_3} = 564 \text{ M}^{-0.15} \text{ s}^{-1}$$

if Maahs's results are used (cf. chapter on in-cloud chemistry). It should be remarked, however, that the measurements were done for 10°C by Penkett and for 25°C by Maahs, and appreciable differences might be expected for lower temperatures.

Once the expressions for v_{gas} and v_{aq} are chosen, equations (13) and (14) should be applied to obtain S_{gas} and S_{aq} . C_{SO_2} in (15) should be obtained using (11), and $[HSO_3^-]$ in (16) or (17), by using (12).

Regarding precipitation, the equilibrium washout assumption discussed in the chapter on scavenging can be extended to scavenging by rain within the cloud (i.e., between z_b and the 0°C level). If the rainfall rate is P , the sink of SO_2 will be

$$S_{pp} = + 10^{-3} \rho_w^{-1} \mu_{SO_2} [HSO_3^-] \frac{dP}{dz} \quad (18)$$

where dP/dz might be assumed to be given by (7). In order to calculate the appropriate value of $[HSO_3^-]$ to introduce in (18), the expression (12) (with $i = SO_2$) cannot be applied directly, because the liquid phase is given not only by the cloud water, i.e. by r_L , but also by the rainwater. Both parts play the same role regarding the solubility equilibrium, as both cloud

droplets and rain drops are assumed in equilibrium with SO_2 in the gas phase. Therefore the mass mixing ratio of rain water should be added to r_L , i.e., a term $P/V\rho$, where V is the falling velocity of precipitation. Thus the concentration in the liquid (rain drops or cloud droplets) in a cloud region containing rain will be

$$[\text{HSO}_3^-] = \frac{X_{\text{SO}_2} H_{\text{SO}_2}^* P}{\rho \left[\frac{\mu_{\text{SO}_2}}{\mu_a} + 10^{-3} \rho_w^{-1} \mu_{\text{SO}_2} \left(r_L + \frac{P}{V\rho} \right) H_{\text{SO}_2}^* P \right]} \quad (19)$$

It may be noticed that $H_{\text{SO}_2}^* = K_1 H_{\text{SO}_2} / [\text{H}^+]$ (K_1 = first dissociation constant).

For V , the following formula, suggested by Scott (1982; App. A) can be applied:

$$V = 3.75 P^{0.11} \quad (20)$$

where P is in mm h^{-1} and V in m s^{-1} .

The total term S for SO_2 will be

$$S = S_{\text{gas}} + S_{\text{aq}} + S_{\text{pp}} \quad (21)$$

Above the 0°C level, the term S_{pp} should be modified by including a retention coefficient γ indicating the fraction of the dissolved SO_2 retained by freezing droplets. It is only known that $\gamma \leq 0.25$ (cf. III.B). The term $P/V\rho$ in (19) should not be included for that cloud region.

b) H_2O_2

All the hydrogen peroxide can be assumed to be dissolved in the cloud water.

There will be a source term S_{pr} representing the production of H_2O_2 in the liquid, as discussed in the chapter on in-cloud chemistry. Following estimates by Chameides and Davis (1982), it was mentioned that the rate of production could be taken as $8.2 \times 10^{-6} \text{ M h}^{-1} = 2.3 \times 10^{-9} \text{ M s}^{-1}$. Thus:

$$S_{pr} = 10^{-3} \rho_w^{-1} \rho \mu_{H_2O_2} r_L \frac{d[H_2O_2]}{dt}$$

$$= 2.3 \times 10^{-12} \rho_w^{-1} \rho \mu_{H_2O_2} r_L \quad (\text{kg m}^{-3} \text{ s}^{-1}) \quad (22)$$

(ρ_w in kg/l).

There will be two sink terms: one due to its reaction with SO_2 and the other to the conversion of cloud to precipitation water.

Using the same expression for the rate of reaction as in (16) or (17), as well as equation (14):

$$S_{aq} = - 10^{-3} \rho_w^{-1} \rho \mu_{H_2O_2} r_L k_{H_2O_2} [HSO_3^-] [H_2O_2] [H^+] \quad (23)$$

where

$k_{H_2O_2}$ has a value as suggested in (16)

$[HSO_3^-]$ is given by (19)

$[H_2O_2]$ is given by (12) with $i = H_2O_2$

$[H^+]$ can be calculated as indicated below (section g)).

The second sink will be given by the rate of conversion of cloud to precipitation water, multiplied by the concentration of H_2O_2 in appropriate units

$$S_{pp} = 10^{-3} \rho_w^{-1} \mu_{H_2O_2} [H_2O_2] \frac{dP}{dz} \quad (24)$$

or, if (7) is used:

$$S_{pp} = -10^{-3} \rho_w^{-1} \mu_{H_2O_2} [H_2O_2] \frac{P_o}{z_{pt} - z_b} \quad (25)$$

(ρ_w in kg/l).

$$\text{Of course, } S = S_{pr} + S_{aq} + S_{pp}.$$

c) O_3

The concentration of O_3 in cloud droplets is given by (9), where $C_{O_3} = C_{O_3,o} = \text{const.}$ (or $C_{O_3}(v) = C_{O_3,o}(v) = \text{const.}$). The only sink term will be given by its reaction with SO_2 . The amount eliminated by precipitation is negligible. Thus

$$S = S_{aq} = -10^{-3} \rho_w^{-1} \rho r_L \mu_{O_3} v_{O_3,aq} \quad (26)$$

where $v_{O_3,aq}$ may be substituted by such expressions as the second terms on the right hand side of (16) or (17).

d) HNO_3

If no in-cloud production of HNO_3 occurs at significant rate, the inflowing HNO_3 becomes immediately dissolved in the cloud, and thereby contributes to the initial value of the term $[A]$, discussed below.

However there is a gas phase oxidation of NO_2 by OH at a rate which may become significant for long-lived stratus systems. There is also in principle the possibility of a heterogeneous oxidation of NO_2 by H_2O_2 . Both reactions were discussed in the chapter on in-cloud chemistry. In any case, the HNO_3 produced would become immediately dissolved and would modify the value of $[A]$.

However, of these two reactions, the former seems only of secondary importance and the latter is entirely hypothetical and will now be ignored. No separate continuity equation is needed for HNO_3 .

e) NO_2

The case of NO_2 is similar to that of O_3 : it is a gas only slightly soluble, so that most of it will remain in gas phase. There will be only one sink term in S, corresponding to its oxidation by OH:

$$S = v_{\text{NO}_2} = -k [\text{NO}_2]_g [\text{OH}]_g \quad (\text{mol m}^{-3} \text{ s}^{-1}) \quad (28)$$

where k is the corresponding rate constant, the brackets indicate concentrations in moles per m^3 of air and a constant concentration of gaseous OH can be adopted as a first approximation.

f) The term $[A]$

As used before (I-10), the term $[A]$ will contain any alkalinity due to the CCN (e.g. CaCO_3 , which in acid pH becomes equivalent to $\text{Ca}(\text{OH})_2$), any acidity also present in the CCN (e.g. H_2SO_4 , NH_4HSO_4), alkalinity or acidity due to initial absorption of gases (NH_3 , HNO_3) and any acidity being produced in the droplets by chemical reaction (oxidation of SO_2). The alkalinity or acidity that may come from particles captured by Brownian motion can be neglected as a secondary effect. $[A]$ can be positive (net alkalinity) or negative (net acidity).

$[A]$ will be given in equivalent-grams of alkalinity per liter of cloud water (i.e., in normality). This alkalinity obviously resides entirely in the liquid phase.

The variable for the continuity equation will be

$$X_A = \rho_w^{-1} \rho r_L [A] \quad (\text{equivalent-grams } \text{m}^{-3}) \quad (29)$$

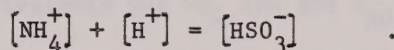
(ρ_w in kg/ℓ). Notice that X_A is given in equivalent-grams per m^3 of air, rather than in kg/m^3 .

To make the meaning of this choice and the following procedure clearer, it may be indicated that the alkalinity or acidity contained in the water acts on the system of equations through the condition of electroneutrality. For pure water, within the simplified treatment (Ch. I, section 10), this equation is

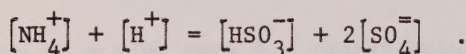
$$[\text{H}^+] = [\text{HSO}_3^-] \quad .$$

If a base such as NH_4OH is considered (assumed totally ionized in solution),

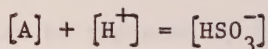
this equation becomes



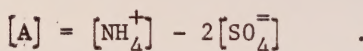
The OH^- ions do not appear, as they have combined with H^+ into H_2O ; they are implicit therefore as a reduction in the value of $[\text{H}^+]$. Similarly, if an acid such as H_2SO_4 is still added, the equation becomes



The added H^+ are implicit as an increase in the value of $[\text{H}^+]$. This equation could be written



where



This is the meaning of the term $[\text{A}]$, which can be trivially generalized to any other case. Added salts, such as Na_2SO_4 , would not alter the equation, as they would simply add equal concentrations of positive and negative charges, which can be cancelled; therefore they do not need to be considered.

The source and sink terms contained in S must now be examined.

There will be a source term S_1 given by the production of both sulfuric acid by oxidation of SO_2 (cf. Chapter II, section 8) and nitric acid by oxidation of NO_2 (see above):

$$S_1 = - (2 \rho_w^{-1} \rho_L v_{\text{SO}_2} + v_{\text{NO}_2}) \quad (\text{equivalent-grams } \text{m}^{-3} \text{ s}^{-1})$$

$$[m] = [m] + [m]$$

The $[m]$ term is not present in the first term because $[m]$ is not a
 the initial condition is a constant in the value of $[m]$. The
 we will not be able to find the initial condition.

$$[m] = [m] + [m]$$

The initial condition is not present in the value of $[m]$. The
 equation will be solved.

$$[m] = [m] + [m]$$

where

$$[m] = [m] + [m]$$

This is the number of the term $[m]$, which can be separated from the
 and after that. After that, we will see the value of $[m]$ and after that
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 be separated from the value of $[m]$ and after that the value of $[m]$ will

$$[m] = [m] + [m]$$

(ρ_w^{-1} in g/l), where v_{SO_2} is the oxidation rate in liquid phase and the number 2 corresponds to 2 equivalents per $SO_4^{=}$ ion and v_{NO_2} has been considered above. v_{SO_2} will be essentially the oxidation in solution by both H_2O_2 and O_3 , for which formulas (16) or (17) can be used. However, if long enough times are involved, as in stratus systems, oxidation in gas phase followed by scavenging by cloud droplets (or nucleation) may be important enough to be also taken into account. v_{NO_2} will only be important in such systems.

There will also be a sink term S_2 , representing the loss to precipitation:

$$S_2 = \rho_w^{-1} \frac{dP}{dz} [A] \quad (\text{equivalent-grams m}^{-3} \text{ s}^{-1}) \quad (31)$$

(ρ_w in kg/l). dP/dz can be replaced by (7), if that approximation is admitted. Notice that dP/dz is negative.

The complete term S is

$$S = S_1 + S_2 \quad .$$

g) H^+

There is no need for a separate continuity equation for H^+ , since its concentration (limited of course to the liquid phase) can be calculated from $[A]$ and from X_{SO_2} or $C_{SO_2,T} = X_{SO_2}/\rho$. $[H^+]$ is given directly by equation (26) from Chapter I, section 10.

h) NH_3

Although this species is important, it will only appear as part of

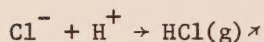
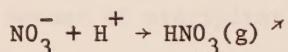
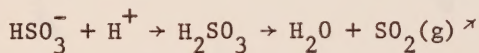
the information needed to obtain the initial value of $[A]$. There is no need to consider a separate continuity equation for NH_3 .

4. Precipitation pH

It is obviously of the utmost importance to be able to estimate the final pH of rain, resulting from the various chemical and physical interactions in the cloud.

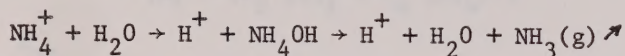
It might seem that the most straightforward approach would be to calculate $\overline{[H^+]}$, averaged over the total rain water. However, this is complicated by the changing solubility equilibrium of SO_2 during the precipitation fall. The parameter $[A]$, on the other hand, does not present that complication, and the final $[H^+]$ can also be calculated from a properly averaged $[A]$.

There is still another circumstance that makes the calculation difficult. If precipitation develops by the ice process, between the 0°C level and the top of the precipitation zone z_{pt} , dP/dz consists of cloud water collected by the riming process. There is an almost total ignorance of the effect of freezing on the chemical composition of cloud droplets. It is to be expected that, due to the phenomenon of segregation (cf. III.B), processes of the type



should occur. It was seen before that 25% might be considered an upper limit

for the retention of SO_2 during freezing of a solution in pure water. How much $[\text{H}^+]$ is lost during riming in a cloud, by processes such as those mentioned above, is not known. Alkalinity could also be lost by a similar process:



but this is less likely to be important, considering that the pH is normally < 7 . The net effect of freezing is thus expected to be a loss of volatile acidity, which will bring the pH of the accreted cloud water to a higher value, once it re-melts. It is obvious that the parameter $[A]$ is changed by this freezing mechanism. In the absence of any experimental information, it is proposed to assume that $[A]$ loses, through freezing, the negative contributions due to all the HSO_3^- present at these levels (taking an average value between $z_{0^\circ\text{C}}$ and z_{pt}), plus all the HNO_3 incorporated from the beginning. The symbol $[A]_f$ will be used to indicate the resulting value.

The situation is simpler between z_b and the 0°C level. The corresponding average of $[A]$ may be calculated from

$$\overline{[A]}_w = \frac{\int_{z_b}^{z_{0^\circ\text{C}}} \rho_w^{-1} \frac{dP}{dz} [A] dz}{\int_{z_b}^{z_{0^\circ\text{C}}} \rho_w^{-1} \frac{dP}{dz} dz} = \frac{1}{P_w} \int_{z_b}^{z_{0^\circ\text{C}}} \frac{dP}{dz} [A] dz \quad (32)$$

where P_w is the amount of precipitation collected by liquid accretion, between z_b and $z_{0^\circ\text{C}}$, and the other symbols have the same meaning as in section 2.

The values of A in the rain falling through z_b will then be given by the total average:

$$\overline{[A]} = (P_f [A]_f + P_w \overline{[A]}_w) / P \quad (33)$$

where $P_f = \int_{z_{00C}}^{z_{pt}} \frac{dP}{dz} dz$ is the amount of precipitation collected by riming, and

$$P = P_f + P_w.$$

As the time spent by precipitation to fall from the cloud base to the ground is relatively short, it may be assumed that $\overline{[A]}$ will not be modified by further SO_2 oxidation. Scavenging of aerosol along that trajectory, however, may alter that value. This effect will be neglected in the following considerations; even in cases when this is not permissible, these considerations should be applicable to precipitation just below cloud base.

The value thus calculated of $\overline{[A]}$ does not depend on the SO_2 solubility equilibrium. As washout of SO_2 is supposed to occur in equilibrium, it may be assumed that C_{SO_2} in the gas phase had the value predominating in the layer above ground, and $[H^+]$ may be calculated from these two parameters ($\overline{[A]}$ and C_{SO_2}). Here the mass conservation equation does not apply, as the external C_{SO_2} is fixed. Thus

$$\begin{aligned} [HSO_3^-] &= \frac{\mu_a}{\mu_{SO_2}} H_{SO_2}^* C_{SO_2} p \\ &= \frac{\mu_a K_1 H_{SO_2}}{\mu_{SO_2}} \frac{C_{SO_2} p}{[H^+]} \end{aligned} \quad (34)$$

where p will be in general ~ 1 atm and K_1 and H_{SO_2} must be taken at ground

temperature. The second equation to be applied is that of electroneutrality; in the simplified treatment,

$$\overline{[A]} + [H^+] = [HSO_3^-] \quad (35)$$

Eliminating $[HSO_3^-]$ from (32) and (35):

$$[H^+] = -\frac{\overline{[A]}}{2} + \sqrt{\frac{\overline{[A]}^2}{4} + Q} \quad (36)$$

$$\text{where } Q = \frac{\mu_a K_1 H_{SO_2} C_{SO_2} P}{\mu_{SO_2}}$$

$$= K_1 H_{SO_2} C_{SO_2}^{(v)} P$$

Example:

Assume, for simplicity, that $[A] = 0$ at the base of the cloud, so that $\overline{[A]}$ is entirely due to the H_2SO_4 formed by oxidation, and assume that it corresponds to half of the inflowing SO_2 transformed into the acid and dissolved in a given r_L . Let $C_{SO_2}^{(v)}$ be the inflowing concentration and also the concentration at the ground.

$$1) \quad C_{SO_2}^{(v)} = 50 \text{ ppv(v)} = 5 \times 10^{-8} \quad ; \quad r_L = 5 \times 10^{-3}$$

$$\overline{[A]} = -2 \times 10^3 \rho_w r_L^{-1} \mu_a^{-1} C_{SO_2}^{(v)} = -3.45 \times 10^{-4} \text{ N}$$

$$[H^+] = 3.47 \times 10^{-4} \quad ; \quad \text{pH} = 3.46$$

whereas if no oxidation occurs ($\overline{[A]} = 0$)

$$[H^+] = 3.16 \times 10^{-5} \quad ; \quad \text{pH} = 4.50$$

$$2) \quad C_{\text{SO}_2}(\text{v}) = 10 \text{ ppb(v)} \quad ; \quad \overline{[A]} = -6.9 \times 10^{-5} \text{ N}$$

$$[\text{H}^+] = 7.18 \times 10^{-4} \quad ; \quad \text{pH} = 4.14$$

$$\text{No oxidation: } [\text{H}^+] = 1.41 \times 10^{-5} \quad ; \quad \text{pH} = 4.85$$

Obviously, a good estimate of $[\text{H}^+]$ and pH of rain will rely on appropriate knowledge of such information as C_{SO_2} at ground, $dP/dz = f(z)$ and the initial value of $[A]$ above the base of the cloud; this last one implies in turn either direct measurement of the cloud water pH at the base or information on the concentration of NH_3 and HNO_3 in the inflowing air and of the chemical characteristics of the aerosol. It is also obvious that the assumptions made above regarding the effect of freezing constitute only a rough approximation of provisional character, as their improvement must await the results of experimental research.

Appendix A. System with $\mathcal{H}_1$, $\mathcal{H}_2$, and $\mathcal{H}_3$ (continued)

From the system of equations (1)-(7), we can be immediately obtained:

$$\mathcal{H}_1 \mathcal{H}_2 = \mathcal{H}_3 \mathcal{H}_2$$

$$\mathcal{H}_1 \mathcal{H}_2 = \mathcal{H}_3 \mathcal{H}_2$$

Using the commutativity of the system parameters, (1) is replaced by (2). The reduced system is then:

$$(a) \quad \mathcal{H}_1 = \frac{(\mathcal{H}_1 \mathcal{H}_2)}{(\mathcal{H}_2 \mathcal{H}_2)}$$

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$$(b) \quad \mathcal{H}_2 = \frac{(\mathcal{H}_1 \mathcal{H}_2)}{(\mathcal{H}_2 \mathcal{H}_2)}$$

$$(c) \quad \mathcal{H}_3 = \frac{(\mathcal{H}_1 \mathcal{H}_2)}{(\mathcal{H}_2 \mathcal{H}_2)}$$

$$(d) \quad \mathcal{H}_4 = (\mathcal{H}_1 \mathcal{H}_2)$$

$$(e) \quad \mathcal{H}_5 = (\mathcal{H}_1 \mathcal{H}_2) + (\mathcal{H}_2 \mathcal{H}_2) + (\mathcal{H}_3 \mathcal{H}_2) + (\mathcal{H}_4 \mathcal{H}_2) + (\mathcal{H}_5 \mathcal{H}_2)$$

Everything can be put in terms of $(\mathcal{H}_1 \mathcal{H}_2) \in \mathcal{H}$. Denote everything in (1) as $\mathcal{H}_1$, and in (2) as $\mathcal{H}_2$, and then the other commutativity and identity relations follow.

Appendix A. System with SO_2 , NH_3 and aerosol alkalinity (cf. I-5).

From the system of equations (1)-(7), two can be immediately eliminated.

$$|\text{H}_2\text{SO}_3| = H_{\text{SO}_2} P_{\text{SO}_2}$$

$$|\text{NH}_4\text{OH}| = H_{\text{NH}_3} P_{\text{NH}_3}$$

These two concentrations are now taken as parameters. Eq. (3) is replaced by $K_1 K_2$. The reduced equation system is now:

$$(2) \quad K_1 = \frac{|\text{H}^+| |\text{HSO}_3^-|}{|\text{H}_2\text{SO}_3|}$$

$$(8) \quad K_1 K_2 = \frac{|\text{H}^+|^2 |\text{SO}_3^{--}|}{|\text{H}_2\text{SO}_3|}$$

$$(5) \quad K_{\text{NH}_3} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

$$(6) \quad K_w = [\text{H}^+][\text{OH}^-]$$

$$(7) \quad \text{Alk} + [\text{H}^+] + [\text{NH}_4^+] = [\text{HSO}_3^-] + 2[\text{SO}_3^{--}] + [\text{OH}^-]$$

Everything can be put in terms of $[\text{H}^+] \equiv X$. Replace everything in (7) in terms of X, solve for X, and then the other concentrations are easily calculated from:

$$[\text{HSO}_3^-] = \frac{A}{X}$$

$$A = K_1 [\text{H}_2\text{SO}_3]$$

$$[\text{SO}_3^{2-}] = \frac{B}{X^2}$$

$$B = K_1 K_2 [\text{H}_2\text{SO}_3]$$

$$[\text{NH}_4^+] = CX$$

$$C = \frac{K_{\text{NH}_3} [\text{NH}_4\text{OH}]}{K_w}$$

$$[\text{OH}^-] = \frac{K_w}{X}$$

Replacing these relations in (7): $\text{Alk} + X + CX = \frac{A}{X} + 2 \frac{B}{X^2} + \frac{K_w}{X}$

or

$$(1 + C) X^3 + \text{Alk} X^2 - (A + K_w) X - 2B = 0 \quad (9)$$

One example of solution is given in Table A1, for a concentration of SO_2

$p_{\text{SO}_2} = 2.7 \times 10^{-8} \text{ atm}$, corresponding to 45 ppb(V) at 0.6 atm, and a concentration of NH_3 $p_{\text{NH}_3} = 6 \times 10^{-9} \text{ atm}$, corresponding to 10 ppb(V) at 0.6 atm.

Table A1

p_{SO_2}	=	$2.7 \times 10^{-8} \text{ atm}$
$[\text{H}_2\text{SO}_3]$	=	$8.9 \times 10^{-8} \text{ atm}$
$[\text{HSO}_3^-]$	=	$1.9 \times 10^{-3} \text{ M}$
$[\text{SO}_3^{=}]$	=	$2.6 \times 10^{-4} \text{ M}$
$[\text{H}^+]$	=	1.5×10^{-6}
pH	=	5.8
p_{NH_3}	=	$6 \times 10^{-9} \text{ atm}$
$[\text{NH}_4\text{OH}]$	=	$1.4 \times 10^{-7} \text{ M}$
$[\text{NH}_4^+]$	=	$2.4 \times 10^{-3} \text{ M}$

It will be observed that the concentration of $[\text{NH}_4^+]$, giving approximately all the NH_3 dissolved, is equivalent to $C_{\text{NH}_3}(\text{V}) = r_L [\text{NH}_4^+]/34.56$ or 3.5×10^{-7} for $r_L = 5 \times 10^{-3}$, or 350 ppb(V). Thus $p_{\text{NH}_3} = 6 \times 10^{-9} \text{ atm}$ or 10 ppb(V) at 0.6 atm is only a minimal part of the total NH_3 remaining undissolved in the gas phase. This illustrates the fact that if the input parameter is the initial concentration in the air, that cannot be restored once the gas dissolved, the calculation must be done in a different manner. This is given in Section 6.

Appendix B. System with SO_2 and NH_3 in amounts limited to an initial input, and aerosol alkalinity (cf. I-6).

Solution of the system of equations (1)-(9) in I-6.

The following variables can be readily eliminated:

$$[\text{OH}^-] = K_w / [\text{H}^+] \quad (8)$$

$$p_{\text{SO}_2} = [\text{H}_2\text{SO}_3] / H \quad (2)$$

$$p_{\text{NH}_3} = [\text{NH}_4\text{OH}] / H_{\text{NH}_3} \quad (6)$$

The reduced system becomes:

$$\begin{aligned} (11) \quad c_{\text{SO}_2, T} &= \left(\frac{\mu_{\text{SO}_2}}{\mu_a \text{PH}} \right) [\text{H}_2\text{SO}_3] + k \{ [\text{HSO}_3^-] + [\text{SO}_3^{=}] \} \\ &= k' [\text{H}_2\text{SO}_3] + k \{ [\text{HSO}_3^-] + [\text{SO}_3^{=}] \} \end{aligned}$$

$$(12) \quad K_1 = \frac{[\text{H}^+] [\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]}$$

$$K_1 K_2 = \frac{[\text{H}^+]^2 [\text{SO}_3^{=}] }{[\text{H}_2\text{SO}_3]}$$

$$(13) \quad K_2 = \frac{[\text{H}^+] [\text{SO}_3^{=}] }{[\text{HSO}_3^-]}$$

$$(14) \quad c_{\text{NH}_3, T} = \left(\frac{\mu_{\text{NH}_3}}{\mu_a \text{PH}_{\text{NH}_3}} \right) [\text{NH}_4\text{OH}] + k_a [\text{NH}_4^+] = k'_a [\text{NH}_4\text{OH}] + k_a [\text{NH}_4^+]$$

$$(15) \quad K_{\text{NH}_3} = \frac{[\text{NH}_4^+] K_w}{[\text{NH}_4\text{OH}] [\text{H}^+]}$$

$$(16) \quad \text{Alk} + [\text{H}^+] + [\text{NH}_4^+] = [\text{HSO}_3^-] + 2[\text{SO}_3^{=}] + \frac{K_w}{[\text{H}^+]}$$

6 unknowns: $[\text{H}_2\text{SO}_3]$, $[\text{HSO}_3^-]$, $[\text{SO}_3^{=}]$, $[\text{NH}_4\text{OH}]$, $[\text{NH}_4^+]$, $[\text{H}^+]$.

From (11), (12), (13') we can obtain

$$[\text{HSO}_3^-] = \frac{K_1 C_{\text{SO}_2, \text{T}}}{k' [\text{H}^+] + k K_1 + \frac{k K_1 K_2}{[\text{H}^+]}} = \frac{K_1 C_{\text{SO}_2, \text{T}} [\text{H}^+]}{k' [\text{H}^+]^2 + k K_1 [\text{H}^+] + k K_1 K_2} \quad (17)$$

$$[\text{SO}_3^{=}] = \frac{K_1 K_2 C_{\text{SO}_2, \text{T}}}{k' [\text{H}^+]^2 + k K_1 [\text{H}^+] + k K_1 K_2} \quad (18)$$

$$[\text{NH}_4^+] = \frac{C_{\text{NH}_3, \text{T}} K_{\text{NH}_3} [\text{H}^+]}{k_a' K_w + k_a K_{\text{NH}_3} [\text{H}^+]} \quad (19)$$

Introducing into (16), we obtain the 5th degree equation in $[\text{H}^+] \equiv X$:

$$\begin{aligned} & k_a K_a k' X^5 \\ & + [k' (\text{Alk } k_a K_a + k_a' K_w + K_a C_{\text{NH}_3, 0}) + k_a K_a k K_1] X^4 \\ & + [\text{Alk } k' k_a' K_w + k K_1 (\text{Alk } k_a K_a + k_a' K_w + K_a C_{\text{NH}_3, 0}) + k K_1 K_2 k_a K_a - \\ & \quad - k_a K_a (k' K_w + K_1 C_{\text{SO}_2, 0})] X^3 \end{aligned}$$

$$\begin{aligned}
& + [Alk \ k \ K_1 \ k_a^I \ K_w + k \ K_1 K_2 (Alk \ k_a \ K_a + k_a^I \ K_w + K_a \ C_{NH_3,0}) - \\
& \quad - k_a \ K_a (k K_1 K_w + 2 K_1 K_2 C_{SO_2,0}) - k_a^I \ K_w (k^I \ K_w + K_1 C_{SO_2,0})] \ X^2 \\
& + [k K_1 K_2 \ Alk \ k_a^I \ K_w - k_a \ K_a \ k K_1 K_2 K_w - k_a^I \ K_w (k K_1 K_w + 2 K_1 K_2 C_{SO_2,0})] \ X \\
& - k_a^I \ k \ K_1 K_2 \ K_w^2 = 0 \quad (20)
\end{aligned}$$

where, for simplicity, K_{NH_3} has been written K_a .

Appendix C. System with SO₂ and NH₃ in amounts limited to an initial input, CO₂ and aerosol alkalinity (cf. I-8).

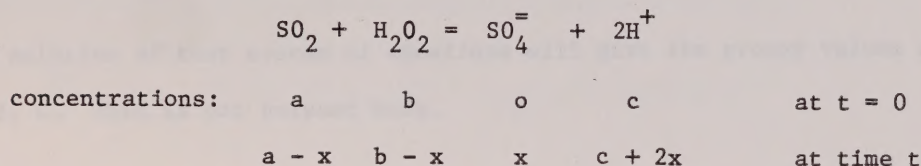
The equation in $X \equiv [H^+]$ is now (instead of the one in Appendix B)

$$\begin{aligned}
 & k_a K_a k' X^5 \\
 & + k_a K_a k K_1 + k' (Alk k_a K_a + k'_a K_w + K_a C_{NH_3,0}) X^4 \\
 & + \{Alk k'_a k'_a K_w + k_a K_a k K_1 K_2 + (Alk k_a K_a + k'_a K_w + K_a C_{NH_3,0}) k K_1 - \\
 & \quad - k_a K_a [K_1 C_{SO_2,0} + k^I \{K_{1C} [H_2CO_3] + K_w\}]\} X^3 \\
 & + \{Alk k_a^I k K_1 K_w + k K_1 K_2 (Alk k_a K_a + k_a^I K_w + K_a C_{NH_3,0}) - \\
 & \quad - k_a K_a [2K_1 K_2 C_{SO_2,0} + k K_1 \{K_{1C} [H_2CO_3] + K_w\}]\} - \\
 & \quad - k_a^I K_w [K_1 C_{SO_2,0} + k^I \{K_{1C} [H_2CO_3] + K_w\}] X^2 \\
 & + Alk k_a^I K_w k K_1 K_2 - k_a K_a k K_1 K_2 \{K_{1C} [H_2CO_3] + K_w\} - \\
 & \quad - k_a^I K_w [2K_1 K_2 C_{SO_2,0} + k K_1 \{K_{1C} [H_2CO_3] + K_w\}] X \\
 & - k_a^I K_w k K_1 K_2 \{K_{1C} [H_2CO_3] + K_w\} = 0 \tag{23}
 \end{aligned}$$

where, for simplicity, K_{NH_3} has been written K_a and K_{1,CO_2} has been written K_{1C} .

Appendix D. Oxidation of SO_2 by H_2O_2 , with limited amount of SO_2 (cf. II.B.1)

The overall reaction of oxidation of SO_2 by H_2O_2 can be written, whatever its mechanism, as



where SO_2 can be identified with total amounts dissolved $\approx [\text{HSO}_3^-]$

Then, at any time t :

$$v = \frac{dx}{dt} = k [\text{H}_2\text{O}_2] [\text{HSO}_3^-] [\text{H}^+]$$

$$= k (a - x)(b - x)(c + 2x)$$

In order to calculate the total amount reacted x , one must integrate between $t = 0$ and $t = \Delta t$ (total time considered):

$$\int_0^x \frac{dx}{(a-x)(b-x)(c+2x)} = k \Delta t$$

The left hand side integral can be solved by the method of rational fractions:

$$\frac{1}{(a-x)(b-x)(c+2x)} = \frac{A}{a-x} + \frac{B}{b-x} + \frac{C}{c+2x}$$

$$= \frac{A(b-x)(c+2x) + B(a-x)(c+2x) + C(a-x)b-x}{(a-x)(b-x)(c+2x)}$$

The numerator is arranged as a polynomial in x , and the coefficients of x^2 and x are set = 0 and the independent term = 1:

$$-2A - 2B + C = 0$$

$$(2b-c) A + (2a - C) B - (a+b) C = 0$$

$$bcA + acB + abC = 1$$

The solution of that system of equations will give the proper values of A, B, C. This is not pursued here.

In any case, the result will be of the form

$$-A \ln \frac{a-x}{x} - B \ln \frac{b-x}{b} + \frac{C}{2} \ln \frac{C+2x}{c} = k \Delta t$$

As the units of k are $M^{-2}s^{-1}$, and those of A, B, C are M^{-2} , everything is divided by, say, $\frac{C}{2}$, so as to have the right-hand side dimensionless, and the equation can be rearranged to the form:

$$\left(\frac{c}{a^{2A/C} b^{2B/C}} \right) \frac{(a-x)^{2A/C} (b-x)^{2B/C}}{c + 2x} = e^{-\frac{2k}{C} \Delta t}$$

For $\Delta t \rightarrow 0$, $x \rightarrow a$ or b , whichever is smaller. The relaxation time for this equation is $= \frac{C}{2k}$.

If it is desired to consider also the HO_2 source, the numerical integration must be performed using the kinetic equation

$$\frac{dx}{dt} = k (a-x)(b-x) + v_0 t (c + 2x)$$

where the term $v_0 t$ represents the continuous source from HO_2 .

Appendix E.

Numerical integration considering H_2O_2 , with continuous source from HO_2 , and simultaneous oxidation by O_3 . SO_2 restricted to initial amount in drops (considered non-replaceable by dissolution from air).

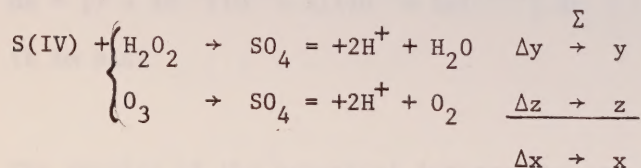
$$\frac{dx}{dt} = k_{H_2O_2} [S(IV)] [H_2O_2] [H^+] + k_{O_3} [O_3] [S(IV)] [H^+]^{-0.4}$$

$$\frac{dx}{dt} = k_{H_2O_2} (a-x)(b-x+z+v_o t)(c+2x) + k_{O_3} [O_3] (a-x)(c+2x)^{-0.4}$$

z

where $v_o t$ represents the continuous reaction with HO_2 .

This is according to (y,z: cumulative contributions of first and second terms):



$$[S(IV)] = a - x$$

$$a = [S(IV)]_o$$

$$[H_2O_2] = b - y + v_o t = b - (x-z) + v_o t$$

$$b = [H_2O_2]_o$$

$$[H^+] = c + 2x$$

$$c = [H^+]_o$$

$$k_{H_2O_2} = 3.1 \times 10^9 M^{-2} \min^{-1}$$

$$[O_3] \approx \text{const. (by}$$

$$v_o = 1.4 \times 10^{-7} M \min^{-1}$$

continuous replenishment

$$k_{O_3} = 1.79 \times 10^4 M^{-0.6} s^{-1}$$

fr. gas phase.

$$= 1.074 \times 10^6 M^{-0.6} \min^{-1}$$

Example:

$$a = b = c = 10^{-5} M$$

$$[O_3] = 6.5 \times 10^{-10} \text{ M (corr. to 50 ppb at 1 atm)}$$

$$k_{O_3}[O_3] = 7.0 \times 10^{-4} \text{ M}^{0.4} \text{ min}^{-1}$$

$$dy/dt$$

$$\frac{dx}{dt} = \overbrace{3.1 \times 10^9 (10^{-5} - x)(10^{-5} - x + z + v_o t)(10^{-5} + 2x)}^{\Delta y} + \frac{dz}{dt}$$

$$\text{with } \frac{dz}{dt} = 7 \times 10^{-4} (10^{-5} - x)(10^{-5} + 2x)^{-0.4} \quad (t \text{ in min})$$

$$\Delta y$$

$$\Delta x = \overbrace{[3.1 \times 10^9 (10^{-5} - x)(10^{-5} - x + z + 1.4 \times 10^{-7} t)(10^{-5} + 2x)]}^{\Delta y} \Delta t + \Delta z$$

$$\Delta z = [7 \times 10^{-4} (10^{-5} - x)(10^{-5} + 2x)^{-0.4}] \Delta t$$

$$(t \text{ in min})$$

The results of the numerical integration are shown in Fig. 1

Appendix F.

Numerical integration considering H_2O_2 , with continuous source from H_2O_2 , and simultaneous oxidation by O_3 . $[S(IV)]$ assumed constant (i.e. the oxidized SO_2 is assumed to be replaced by dissolution from the atmosphere).

$$\frac{dx}{dt} = k_{H_2O_2} a(b - x + z + v_o t)(c + 2x) + z$$

$$z = k_{O_3} a[O_3](c + 2x)^{-0.4}$$

Numerical constants as in Appendix E.

Example:

With values assumed before ($c = b = c = 10^{-5}$) (Appendix)

$$k_{H_2O_2} a = 3.1 \times 10^4$$

$$k_{O_3} a[O_3] = 7 \times 10^{-9}$$

$$\Delta x = [3.1 \times 10^4 (10^{-5} - x + z + 1.4 \times 10^{-7} t)(10^{-5} + 2x)] \Delta t + \Delta z$$

$$\Delta z = [7 \times 10^{-9} (10^{-5} + 2x)^{-0.4}] \Delta t \quad (t \text{ in min})$$

The results of the numerical integration are shown in Fig. 2.

Appendix G. Oxidation of SO_2 by O_3 in a cloud. Approximation taking into account equilibrium between liquid and gaseous phases (cf. II.9).

For this order-of-magnitude estimate, a number of simplifications will be made:

- H_2O_2 will not be considered, which is equivalent to assuming that its concentration is 0.
- $P_{\text{NH}_3} = 0$.
- $\text{Alk} = 0$ (the aerosol, in particular the cloud condensation nuclei, is assumed to be neutral).
- $p = 0.6 \text{ atm}$, taken as a constant.
- $[\text{O}_3]$ will be taken as a constant, although an equivalent part to the oxidized SO_2 should disappear. This is done to simplify the computation, and should not alter essentially the results. The concentration taken will be equivalent to 50 ppb(v) at 0.6 atm ($\text{H}_{\text{O}_3} \approx 2.18 \times 10^{-2} \text{ M atm}^{-1}$, value for 0°C): $[\text{O}_3] = 6.5 \times 10^{-10} \text{ M} = \text{const.}$
- $r_L = 2.5 \times 10^{-3}$.
- Equilibrium conditions will be assumed to be maintained, i.e., these conditions are rearranged instantaneously, as the reaction takes place.
- Reaction rates valid at 25°C (see later) are mixed with other 0°C conditions.

The three equations used will be:

reaction:
$$v = \frac{d[S(VI)]}{dt} = k [O_3] [HSO_3^-] [H^+]^{-0.85} \quad (1)$$

$$k = 3.38 \times 10^4 \text{ if } v \text{ is given in } M \text{ min}^{-1}.$$

This equation is fitted to represent the results of Maahts (1983) (see his Fig. 1), which are not far from Erikson's and higher than Penkett's, but approximately coinciding with both for low pH (3-4). These results are valid for 25°C (no data at 0°C are available), while here the computation is done for approximately 0°C; this inconsistency, however, is not expected to invalidate the order-of-magnitude estimates, or the general conclusions.

For $[O_3] = 6.5 \times 10^{-10} M$, $v = 2.2 \times 10^{-5} [HSO_3^-] [H^+]^{-0.85}$ (1')

solubility:
$$\begin{aligned} [S(IV)] &\approx [HSO_3^-] = \frac{K_1 [H_2SO_3]}{[H^+]} \\ &= \frac{K_1 H_{SO_2}^P SO_2}{[H^+]} = \frac{K_1 H_{SO_2}^C SO_2(V)}{[H^+]} \quad p \\ &= 5.3 \times 10^{-2} \frac{C_{SO_2}(V)}{[H^+]} \end{aligned}$$

(where $K_1 = 3.1 \times 10^{-2} M$, $H_{SO_2} = 2.85 M \text{ atm}^{-1}$ were used).

mass conservation: $10^{-3} \rho_w^{-1} \mu_a r_L [\text{HSO}_3^-] + c(V) = c_T(V)$ (3)

where $c_T(V)$ = equivalent volume mixing ratio for the total SO_2 both gaseous and dissolved.

$c(V)$ = volume mixing ratio in gas phase alone.

Equation (3) can be written ($\rho_w = 1 \text{ g cm}^{-3}$, $\mu_a = 29 \text{ g mol}^{-1}$):

$$7.24 \times 10^{-5} [\text{HSO}_3^-] + c(V) = c_T(V) \quad (4)$$

and combining with (2):

$$c(V) = \frac{c_T(V)}{1 + \frac{3.84 \times 10^{-6}}{[\text{H}^+]}} \quad (5)$$

(time in min).

The reaction is: $\text{HSO}_3^- + \text{O}_3 \rightarrow \text{SO}_4^{=2-} + \text{H}^+ + \text{O}_2$

$t = 0 :$ a 0 b

$t = t :$ $a-x$ x $b+x$

where

$$a \equiv [\text{HSO}_3^-]_0$$

$$b \equiv [\text{H}^+]_0$$

The integrating procedure is:

$$1. \text{ Initial conditions} \quad - \quad [\text{HSO}_3^-]_0 = a$$

(see also below)

$$[\text{H}^+]_0 = b$$

$$c_{\text{T}}(\text{V}) = c_{\text{T},0}(\text{V}) = 10^{-8} \quad (10 \text{ ppb}(\text{v}))$$

$$c_{\text{SO}_2}(\text{V}) = \frac{c_{\text{T},0}(\text{V})}{1 + 3.84 \times 10^{-6} \frac{1}{a}}$$

$$2. \Delta_1 x \text{ obtained from (1')}$$

$$(v = \frac{dx}{dt} \approx \frac{\Delta x}{\Delta t}) : \Delta_1 x = 2.2 \times 10^{-5} [\text{HSO}_3^-]_0 \text{H}^+{}^{-0.85}_0 \Delta_1 t$$

$$3. [\text{H}^+]_1 = a + \Delta_1 x$$

$$4. c_{\text{T},1}(\text{V}) = c_{\text{T},0}(\text{V}) - 7.24 \times 10^{-5} \Delta_1 x \quad (\text{from (4)})$$

$$5. c_1(\text{V}) = \frac{c_{\text{T},1}(\text{V})}{1 + 3.84 \times 10^{-6} \frac{1}{[\text{H}^+]_1}} \quad (\text{from (6)})$$

$$6. [\text{HSO}_3^-]_1 = 5.3 \times 10^{-2} \frac{c_1(\text{V})}{[\text{H}^+]_1} \quad (\text{from (2)})$$

Repeat 1-6 with new values, etc.

For the initial conditions, if cloud water is pure, $a = b = 2.1 \times 10^{-5} \text{ M}$,

$$c_{\text{SO}_2,0}(\text{V}) = 8.4 \times 10^{-9}.$$

If cloud water has an initial pH = 4.0, $a = 5.1 \times 10^{-6} \text{ M}$, $b = 10^{-4} \text{ M}$,

$$c_{\text{SO}_2,0}(\text{V}) = 9.63 \times 10^{-9}.$$

This procedure was applied to two examples:

Example 1 - Cloud water is assumed initially pure.

Input concentration of SO_2 in the air $c_{\text{T},\text{o}}(\text{V}) = 10 \text{ ppb}(\text{v})$.

Example 2 - Cloud water is assumed to have an initial $\text{pH} = 4.0$.

Other conditions as in Example 1.

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